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Rotatory Power of Optically Active Benzoic Esters containing Ionisable Ortho- Substituents.

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Optical Activity of Electrolytes.

Introduction.

Among the many and varied fields of present day chemistry, that of optical activity occupies a not unimportant position. The foundation of this section of the science was laid by Malus, who, in 1808 discovered the phenomenon of polarised light. In 1811 Arago observed that the plane of polarisation was rotated by quartz and in 1815 Biot's researches resulted in the discovery that solutions of certain organic substances, such as cane sugar, possessed a similar power. The significance of Biot's discovery was quickly realised and subsequently many researches on the optical activity of organic compounds were commenced.

It soon became obvious that the specific rotation of a substance in solution is controlled by various factors. The elucidation of the significance of these factors is due to Biot, Gernez etc., who showed that the specific rotation of a substance in solution is dependent upon the temperature and concentration of the solution and the nature of the solvent.

In 1860,[1.] Biot published a summary of all his works, stressing the different influences controlling

the rotations of substances in solution. However, in 1877,[2] Landolt drew attention to the fact that many of the previous workers had paid little or no attention to the concentration of the solutions examined and in the light of later work extended Biot's results.

Although[3] Biot had observed that the addition of acids to aqueous solutions of tartaric acid resulted in a diminution of the rotation, the knowledge of the conditions influencing the optical activity of electrolytes was very meagre, when in 1873[4] Landolt carried out a complete investigation of tartaric acid, its esters and its salts. He found that the normal salts all had approximately the same molecular rotation in 0.5 M solutions.

Molecular Rotations of Metallic Tartrates in 0.5 M Solutions.

Salt.	$[M]_D$
Li.Li.	+58.06°
$NH_4.NH_4$.	+63.04°
Na.Na	+59.85°
K.K.	+64.42°
NH_4.Na	+61.71°
NH_4.K.	+63.81°
Na.K.	+62.34°
Mg	+61.68°

In 1876, Oudemans Jr.[5] made an examination of the rotations of various salts of the cinchona alkaloids, the purpose of the investigation being to find if it was possible to use the optical activity

of these substances as a means of analysis. No results of immediate value were obtained, but in 1879,[6.] during the progress of a research on the alkaloid Quinamine, he found that the rotations of the various salts were approximately the same in 0.05 M solutions.

Rotation of Quinamine Salts in 0.05 M Solutions.

Salt.	$[\alpha]_D$
Q.HCl	+114.4°
Q.HNO_3	116.5°
Q.$HClO_3$	116.1°
Q.CH_3COOH	116.2°
Q.HCOOH	114.7°
Q.$\begin{matrix}COOH\\COOH\end{matrix}$	116.1°
Q.H_3PO_4	117.3°

Q = Quinamine.

Oudemans' results were thus in agreement with those previously published by Landolt. The culmination of the work was the statement of the Oudemans' Law:-

"The specific rotation of the alkaloids is modified to the same extent by different acids."

Oudemans[7.] later extended his work by investigating the case of the different salts of the same optically active acid, a research similar to that of Landolt on the tartrates. His results for the salts of quinic and podocarpic acids showed that the Oudemans' Law held in this case also.

The work of later authors has served to confirm the Oudemans' Law. Thus Hadrich[8], in 1893, summarised the work of Landolt and Oudemans; he then investigated the rotations of salts of a number of optically active strong bases at different concentrations. His results were in harmony with those of Oudemans. In the same year Kipping and Pope[9] prepared α-bromocamphor.π. sulphonic acid, and carried out an investigation on the rotatory power of the acid and its salts. From a consideration of his own results and those of Kipping and Pope, Hadrich extended the Oudemans' Law.

"The rotations of optically active electrolytes tend towards a definite value as the dilution is increased, and this value is independent of the inactive ion."

Hadrich further proposed that the law was a necessary consequence of the dissociation theory, which had been advanced some years previously by Arrhenius.

The explanation of the Oudemans' Law on the basis of the theory of electrolytic dissociation may be summarised briefly in the following manner.

Consider the case of an optically active electrolyte in solution. On the Arrhenius theory the optically active molecule is dissociated into ions, one of which is optically active, the other inactive. This we may represent in the following manner: $AB \rightleftarrows \overset{+}{A} + B'$,

AB being the undissociated molecule, A^+ the inactive ion and B' the active ion. It may be regarded as very probable that the rotatory power of the undissociated molecule differs from that of the active ion, B'. In moderately concentrated solutions the rotatory power will depend not only upon the rotation of the undisscciated molecule, but also upon that of the active ion. As the solution is diluted the proportion of undissociated molecules will decrease, the rotatory power showing a corresponding change. The limit is reached in the case of very dilute solutions, when the quantity of undissociated molecules is negligible. In such solutions the specific rotation is dependent entirely upon the concentration of the active ion, and will be independent of the nature of the inactive ion.

The figures quoted by Landolt and Oudemans show rotations which are not quite constant. On the dissociation theory, these variations would be explained on the grounds of the presence of undissociated molecules in the concentrations considered.

In view of the more recent work on the nature of dissociation, it is interesting to consider the Oudemans' Law in the light of the theory of complete dissociation.

Consider, as before, the case of an optically active electrolyte in solution. On the complete dissociation theory, the rotatory power of the electrolyte is due entirely to the active ion, since

there are no undissociated molecules to be considered. In this case the change in rotatory power with change of concentration is explained as being due to the effect of the inactive cation on the active anion. The ions being electrical systems, it may be regarded as probable that the proximity of the cation to the active anion will have a definite effect on the configuration of the latter: that this will affect the rotatory power of the active anion is to be expected. The rotation of the active anion (and therefore of the solution) may be considered as being dependent upon the nature of the ionic atmosphere surrounding the active ion and also upon the concentration of the electrolyte in solution. With dilution, the limiting case is reached when the active anion is no longer appreciably affected by the surrounding ions; in such solutions the rotation is independent of the nature of the positive ion.

The results leading to the formulation of Oudemans' Law were all obtained in dilute solution. (1/40 M - I/2 M). That the law holds in dilute solutions and in dilute solutions only, has been shown by later authors: eg., Schneider[10.]'s work on the salts of malic acid and more recently the work of Darmois[11.] on the tartrates. The law has suffered some criticism, various investigators having pointed out that it is only approximately obeyed.

Thus, Shinn[12.], who repeated and extended the

work of Hadrich, concluded that "the rotations of the salts studied (salts of alkaloids) do not tend to become identical for salts containing the same active base." Furthermore, Shinn could not bring his results into harmony with the theory of electrolytic dissociation.

Stubbs[13] has also pointed out that the salts of malic acid do not obey the Oudemans' Law.

Salts of Malic Acid.

Molecular rotations at infinite Dilution.

Salt	$[M]_D$
K_2	-15.5°
Na_2	-16.2°
Li_2	-19.2°

The rotations at infinite dilution were obtained by graphical extrapolation. Stubbs summarises as follows: "At infinite dilution the influence of the metallic ion persists, for, unlike the case in which the ions of electrolytes influence malic acid by their chance proximity, the positively charged cation must by electrostatic forces be kept always within the sphere of influence of the negatively charged active anion."

The case of the effect of added electrolytes will be discussed later, but the explanation in the

case of the salts would appear to be somewhat at variance with the significance ordinarily attached to the term "infinite dilution".

An investigation of interest at this point was made by Walden[14], who made a very accurate study of the salts of α-bromocamphor.π.sulphonic acid, this acid being chosen since it had a rotation sufficiently great to allow of accurate measurements in extremely dilute solution. In addition the degrees of dissociation of the various salts were measured at the different concentrations. The following is a summary of Walden's results.

Acid or Salt	V.	$[M]_D$	m.
Acid	2.08	+287°	68.5%
	60	269°	94.4%
Li.	"	272°	–
Na.	"	272°	86.8%
K.	"	269°	87.2%
Tl.	"	272°	87.3%
Be/2	"	272°	77.3%
Mg/2	"	270°	–
Zn/2	"	269°	77.2%
Ba/2	"	271°	74.8%

V = vol. containing 1 gm. equivalent of acid or salt.

m = degree of dissociation - calculated from conductivity data.

The above results would appear to be somewhat anomalous, since whereas the conductivity data indicate approximately 70 - 90% dissociation, the molecular rotations of the various salts appear to be consistent with complete dissociation.

15. Noyes has avoided this difficulty, his assumption being that in solution there are two types of molecules:

$A^+ \cdots\cdots B'$	$A — B$	····· Weak bonds
Electrical Molecule.	Chemical Molecule.	— Strong "

In the case of salts, undissociated molecules exist largely as electrical molecules. As shown by conductivity measurements, the molecule is undissociated, but the optical activity of the molecule is the same as that of the free ion, since the ion exists in the molecule as a "latent ion".

16. More recently, Walden has measured the molecular rotations of tetra.ethyl-ammonium α-bromo-camphor.π.sulphonate. He finds that in solutions more dilute that 1 gm.mol./17 litres, the molecular rotation is independent of the concentration. Walden explains the constancy of the molecular rotation on the basis of Noyes' theory, thus assuming the presence of undissociated molecules at the concentrations in question.

17. The work of Rimbach on the optical activity of rubidium tartrate rather leads to the idea that a simpler explanation of Walden's results would be based on the theory of total dissociation at the concentrations considered. Thus in dilute solutions conductivity measurements gave the degree of dissociation as 72.9%. By use of the formula

$$m = \frac{[\alpha] - [\alpha]_0}{[\alpha]_\infty - [\alpha]_0}$$

m is the degree of dissociation
$[\alpha]$ – specific rotation of the solution examined.
$[\alpha]_0$ – specific rotation at infinite concentration.
$[\alpha]_\infty$ – specific rotation at infinite dilution.

Rimbach obtained the value m = 97.7%, a figure much more in agreement with the present idea of dissociation in dilute solution.

A valuable contribution to the knowledge of the factors influencing the rotatory powers of solutions with change in concentration was made by G.H. Schneider[18] in 1881. This author made a very complete examination of the rotatory power of the malates and hydromalates of Lithium, Sodium, Potassium and Ammonium in aqueous solution. Barium Malate was also examined. The specific rotations of the various salts were plotted against the concentration in aqueous solution. On the same graph, the variation of the rotatory power of malic acid with concentration was given; the concentration effect, as is well known, is to cause a change from l-rotation in dilute solution to d-rotation in the more concentrated solutions. The salts undergo changes precisely similar to the above, the effect of concentration being to change the original l-rotation in the d-direction. The curve for the barium malate differs somewhat from those for the other salts, the change in rotation with concentration being much more rapid.

The following is a short summary of the various results.

Acid or Salt.	$[\alpha]_D$ for pure substance.	$[\alpha]_D$ at infinite dilution.	$[\alpha]_D$ in 20% solution.
Malic acid	+5.89°	-3.07°	-1.28°
Lithium Malate	+26.72°	-12.71°	-9.43°
Ammonium "	-3.32°	-8.93°	-6.99°
Sodium "	+15.20°	-9.84°	-6.14°
Potassium "	+3.02°	-7.31°	-6.13°

19.

Stubbs, who has made a study of Schneider's figures, comments as follows:-

"He found the specific rotation of malates to vary with the concentration, even more so than with malic acid itself. Moreover, the diversity of rotation shown by the various malates is not merely due to his plotting specific rotations against percentage composition of the solutions, for when calculations are made from his data and molecular rotations plotted against molar concentrations, the diversity persists in a no less striking form."

Indeed, in the case of the malates, the molecular rotation at infinite dilution of the potassium salt is more dextro than that of the sodium salt, and the latter than that of the lithium salt, an order of effect remarkably parallel to that given by Stubbs for the addition of alkali salts to malic acid in aqueous solution.

A line of research which has proved of great

value in connection with optically active electrolytes is the addition of salts to solutions of the optically active substance. Thus, Biot[20] in 1837 observed that the specific rotation of tartaric acid was greatly increased by the addition of boric acid. The work of Gernez[21] showed that salts of molybdenum had a remarkably large effect on the rotation of the same acid. Many similar results were observed and the effects were accounted for by the assumption that complex additive compounds were formed.[22]

Of more interest here, however, is the effect of the common inorganic salts. The influence of inorganic salts has been studied in the case of certain active sugars by several workers e.g., Farnsteiner,[23] Rimbach[24] and Wender.[25] The effects generally are small, increase with increasing salt addition and in some cases show regularities according to the periodic system.

Long[26] has investigated the effect of the addition of the alkali halides to solutions of sodium and potassium tartrates. He found that potassium and ammonium salts raised the rotation, while sodium, lithium and thallium salts lowered it.

Stubbs[27] has made a very thorough investigation of the influence of inorganic salts on the rotation of *l*-malic acid. A very comprehensive list of salts has been employed, these being added to

1.5 M solutions of the acid and the difference in specific rotation of the solutions observed. The following tables give the results observed for the addition of salts of monovalent and divalent metals.

Salts of Alkali Metals.

Salt added	n	△	Salt added	n	△
CsCl	1/4	1.94°	NH_4Cl	1/4	1.16°
CsCl	1	4.66°	NH_4Cl	1	3.28°
RbCl	1/4	1.95°	LiCl	1/4	0.73°
RbCl	1	5.08°	LiCl	1	2.84°
KCl	1/4	1.95°	KI	1/4	2.39°
KCl	1	5.57°	KBr	"	2.11°
NaCl	1/4	1.67°	KCl	"	1.95°
NaCl	1	5.39°	KNO_3	"	1.88°
			K_2SO_4	"	1.48°

Barium and Calcium Salts and Salts of weaker Bases.

Salt added	n	△	Salt added	n	△
$BaCl_2$	1	17.23°	$Cd(NO_3)_2$	1/4	0.73°
$BaCl_2$	1/4	5.58°	$ZnCl_2$	"	0.56°
$Ba(NO_3)_2$	"	4.83°	$MgCl_2$	"	0.77°
$CaCl_2$	"	3.95°	$AlCl_3$	"	0.60°
$Ca(NO_3)_2$	"	3.69°			
$HgCl_2$	1/5	0.36°			

n = no. of equivalents of salt added.
△ = observed difference in specific rotation between solution of acid and solution of acid + salt.

The effect of the salts is to change the ℓ-rotation of the acid in the dextro direction. From the above tables and other figures, Stubbs arranges the ions in order of their influence on the rotation. From the figures for the alkali metals, the following series are deduced for the cations and anions.

$$Cs^{+} > Rb^{+} > K^{+} > Na^{+} > NH_4^{+} > Li^{+} > H^{*}$$

$$I^{-} > Br^{-} > Cl^{-} > NO_3^{-} > \tfrac{1}{2}SO_4^{--}$$

The following is the order of influence of the other metals examined.

$$Ba^{++} > Ca^{++} > Mg^{++} > Cd^{++} > Al^{+++} > Zn^{++} > Hg^{++}$$

Barium and Calcium salts are seen to have a specially great influence on the rotation of the acid.

From a general consideration of his results, Stubbs concludes that the main influence is probably exerted by the positive radicle; also that the influence is mainly a specific additive property of the ionsor radicles and appears to be related to the valency of the ions and their order of electro-affinities.

The author dismisses as most improbable the theory that the changes are due to the formation of complexes. Among the reasons cited against this theory are

1) The regular nature of the salt influence

& 2) the à priori inconceivability of a salt such as KCl forming such complexes.

The dehydration theory is also rejected.

* It was found that HCl exerts a less influence than does LiCl, so that the order of influence is $K > Na > Li > H$, parallel to the order of atomic weights.

"An explanation plausible at first sight is that the formation in solution of hydrated molecules by the added salts would act like concentrating the solution, which is well known to influence the rotation of malic acid in a dextro-sense."

The evidence against such a theory is strong. In the first place, the magnitude of the salt influence is often far too great to be explained in the above manner, $BaCl_2$, for example, producing at the higher concentration an effect several times as great as would be given by total dehydration of the malic acid. (assuming Schneider's value of $+5.89°$ for the rotation of the anhydrous acid.) Secondly, in general, the salts with the greatest affinity for water, e.g., LiCl, exert the least influence.

From general considerations, among which may be mentioned "the smallness of the effect of mercuric chloride and acetic acid, the two practically non-ionised substances used" and also " the parallelism between unexpectedly low influence and low conductivity in the case of barium nitrate", Stubbs finally concludes that the effects observed are chiefly produced by the ions. The nature of the ionic influence is little more than surmised, the suggestion being put forward that it may be connected with the sensitiveness of the hydroxyl group in malic acid.

It is worthy of note that when the hydroxyl group of malic acid is attacked and a chemical complex formed, the great sensitiveness of the acid to concentration disappears.[28]

Patterson and Anderson[29] have carried out a research somewhat similar to that of Stubbs. The case investigated was the effect of salt addition to aqueous solutions of ethyl tartrate. The following is a summary of the results obtained.

Effect on the rotation of a 0.5 M aqueous solution of Ethyl Tartrate by the addition of various salts.

Salt added	M	△
$BaCl_2$	2	-12.43°
NH_4Cl	"	- 3.81°
NaCl	"	- 6.05°
KCl	"	- 6.78°
NH_4NO_3	"	- 3.87°
$NaNO_3$	"	- 7.31°
KNO_3	"	- 7.03°
NaI	"	-10.11°
KI	"	- 9.68°
NaBr	"	- 6.51°
KBr	"	- 7.96°

M = molarity of added salt.

△ = observed change in specific rotation.

The effect of the salt addition is to change the original d-rotation in the ℓ-direction. The effects undoubtedly show a remarkable similarity to those obtained by Stubbs; the large effect of $BaCl_2$ and the series $K > Na > NH_4$ for the chlorides being exactly analogous to the changes observed in the case of malic acid.

The dehydration theory is discussed, the authors concluding that their results strongly support the views of Stubbs on this point.

The effect of salts on the homogeneous ester was also investigated, the authors finding that similar effects to those quoted above are obtained.

The possibility of combination between the salts and the ester is discussed, but it is concluded that "since there is nothing to show that the influence of inorganic salts is of a different order from that of organic solvents, and as no evidence of any weight has hitherto been brought forward in favour of combination in the latter, better investigated case, there seems no valid reason for assuming it in the former either."

In view of the fact that the regularities obtained in the case of aqueous solutions are also evident in the case of the homogeneous ester , although to a lesser degree, it is concluded that "it seems improbable that ionisation plays any important part in the matter."

Recently, Darmois[30] has studied the rotatory powers of neutral tartrates in aqueous solution and in neutral salt solutions. The following are his results for the alkali tartrates in aqueous solution. The measurements for rubidium tartrate are due to Rimbach.[31]

Tartrate	Rotatory Powers of Alkali Tartrates in Aqueous Solution					
Lithium	c	0.425	0.85	0.973	1.70	1.82
	$[\alpha]_J^{T''}$	39.9°	38.5°	38.1°	35.3°	34.6°
Sodium	c	0.174	0.348	0.653	0.87	1.303
	$[\alpha]_J^{T''}$	42.3°	42.0°	41.5°	41.2°	40.3°
Ammonium	c	0.20	0.50	0.65	1.00	1.30
	$[\alpha]_J^{T''}$	44.1°	44.6°	44.8°	45.05°	45.3°
Potassium	c	0.255	0.51	1.02	1.70	2.55
	$[\alpha]_J^{T''}$	44.9°	45.5°	46.5°	47.2°	48.3°
Rubidium	c	0.166	0.346	0.738	1.723	2.68
	$[\alpha]_J^{T''}$	44.8°	45.25°	46.4°	49.2°	51.2°
Caesium	c	0.24	0.68	1.00	1.21	1.40
	$[\alpha]_J^{T''}$	44.45°	45.8°	47.0°	47.65°	48.25°

c is the concentration in gm.mols./litre. $[\alpha]_J^{T''}$ is deduced from the specific rotatory power by use of the formula $[\alpha]_J^{T''} = [\alpha]_J \cdot \frac{\text{M.W. of salt}}{\text{M.W. of tartrate ion.}}$

From the above it is seen that the rotatory power of the ammonium, potassium, rubidium and caesium tartrates increases with concentration, while the

rotatory power of the lithium and sodium tartrates shows a decrease.

By drawing the various curves on a single graph, Darmois obtains an interesting regularity. "The curves are in the order Li, Na, K, Rb, Cs; this is the order of ionic radii calculated from ionic mobility with the aid of Stokes' formula; these radii are:-

Li.	Na.	K.	Rb.	Cs.	
2.30	1.79	1.22	1.17	1.17	Å."

Darmois assumes that the tartrates are completely dissociated at all the concentrations considered and supposes that with increasing concentration, the tartrate ion undergoes a modification related to the radius of the cation of the tartrate. This is in accordance with the work of Fajans,[32] which shows that, in general, the anions undergo deformation under the influence of the more compact cations. This modification is assumed to be produced by the electric field of the cation, the maximum therefore being reached in the case of Rubidium and Caesium. The deformation effect being assumed to increase the rotatory power of the salts studied, a second effect must be admitted, since in some cases the rotatory power decreases with concentration. To account for this result, Darmois supposes that the tartrate ion is hydrated in solution and undergoes a partial dehydration in the more concentrated solutions. In the case of Lithium and Sodium tartrates, this "dehydration effect"

is so great as to overcome the opposing "deformation effect", the rotatory power of the tartrates in question decreasing with concentration. From a study of the tartrates of organic bases, Darmois brings forward some results in support of his hypothesis. Thus the rotatory power of benzylamine tartrate increases rapidly with concentration; this is assumed to be a consequence of the fact that the benzylamine ion is not hydrated. On the other hand, the rotatory power of tetraethylammonium tartrate decreases greatly with concentration. On Darmois' theory, this is accounted for by the fact that the $[N(C_2H_5)_4]^+$ ion is hydrated in solution.

The effect of neutral salts is studied by measuring the rotatory power of sodium tartrate in various chloride solutions. The results serve to confirm the effects obtained with the alkali tartrates, sodium and lithium chlorides decreasing the rotation, while potassium chloride causes an increase. $MgCl_2$ and $CaCl_2$ cause even a greater decrease than does LiCl, this effect being accounted for by the dehydration theory.

Arranged in order of their influence on the rotation, the following series is obtained:

$$K^+ < Na^+ < Li^+ < Mg^{++} < Ca^{++}$$

$ThCl_4$ gives at once a considerable increase, due to the great field of the Th^{++++} ion. The divalent cations of the heavy metals (Mn, Fe, Hg) are also

situated on the side corresponding to deformation.

Darmois accounts for the results obtained with the above cations as being due to the formation of associated compounds, this also holding in the case of Zn, Cd, and Cu.

The rotatory power of ethyl tartrate in aqueous solution and in several solutions of electrolytes has also been studied, the various solutions being considered as solvents in which the concentration of ethyl tartrate is varied. Concentration of the aqueous solution of the tartrate causes a shift in rotation towards the laevo-side. In this case, all the salts studied decrease the rotation; this holding even in the case of potassium chloride, which gave an increase with the inorganic tartrates. The effect of KCl is, for a given concentration, greater than that of LiCl, but very much smaller than that of $CaCl_2$. Darmois reaches no definite conclusions with regard to the ethyl tartrate values.

The results generally are of great interest, significant regularities being obtained. The dehydration theory advanced has provoked some criticism, but, with regard to this, it seems to the present writer that Darmois has scarcely been met on his own ground. This point will be more fully discussed later.

Of interest at this point is a paper published by Levene and Rothen,[33.] part of which is devoted to a study of the effect of addition of neutral salts

to Mandelic acid. The effect was studied with reference to the undissociated acid and the ion. Thus the experiments were carried out at two definite pH's, in order to ensure that the observed effect was a pure salt effect and could not be attributed to changes in the ionisation. One series was made on the slightly alkaline side, mandelic acid being neutralised first by one equivalent of sodium hydroxide, and another series on the acid side, by adding one equivalent of HCl to the solution. The pH's of the solutions were checked to ensure the presence in solution of either the undissociated molecule or the ion.

The results are summarised in the following tables:-

Effect of neutral salts on the rotation of the Mandelate ion.

Salt added	n	$[M]_D^{25^\circ}$
LiCl	0.4	180.2°
NaCl	"	178.9°
KCl	"	179.5°
RbCl	"	179.2°
$CaCl_2$	"	235.0°
$SrCl_2$	"	197.2°
$BaCl_2$	"	198.8°
$(NH_4)_2SO_4$	"	179.6°
K_2SO_4	"	178.3°
-	-	176.7°

Effect of neutral salts on the rotation of the undissociated Mandelic acid.

Salt added	n	$[M]_D^{25^\circ}$
LiCl	0.09	238.1°
NaCl	"	237.6°
KCl	0.4	238.7°
$CaCl_2$	"	253.5°
$SOCl_2$	"	252.2°
$BaCl_2$	"	252.0°
$(NH_4)_2SO_4$	"	232.6°
K_2SO_4	"	232.0°
$ZnSO_4$	"	231.1°
-	-	237.3°

n is the concentration of salt in mol.per litre.

The concentration of mandelic acid is in all cases app., 0.05 M.

As may be seen from the figures, all the neutral salts studied, (with the exception of the sulphates) have a positive effect - the rotation is increased. Here, as in other cases, the charge on the salt ion plays an important role, divalent ions having a much greater effect than monovalent ions.

So far as series effect is concerned, the results are the exact antitheses of those obtained by Stubbs, in the case of malic acid. Thus the authors find that the effect decreases with the alkaline earth metals in the series Ca > Sr > Ba, whereas Stubbs found that barium had a much greater effect than calcium. In the case of the alkali series, lithium produced a greater effect than rubidium, but there is no apparent regularity for the intermediate metals. This again is at variance with Stubbs' results, who found that lithium produced a smaller effect than rubidium.

In the case of the undissociated mandelic acid, rather an unexpected result is observed. "We have seen that in the neutral salt effect, the influence of the cation, (whatever its charge and size) predominates over that of the anion upon the change of rotation of mandelate ion, this being due to the negative charge of the latter. In the case of mandelic acid we are dealing with a neutral molecule and the predominant action of one ion on the other is then due only to their respective charge, size and structure. The

resulting effect ought to be less than in the case of the mandelate ion and in an opposite direction (-ve) when the influence of the anion is predominant."

The above statement is borne out by the results; in the case of mandelic acid, for every sulphate studied (except $Al_2(SO_4)_3$) there is a decrease in the molecular rotation of the acid, the effect of the doubly charged SO_4" ion being predominant. In the case of the mandelate ion, the effect of the sulphates studied is to raise the rotation. That the effects observed are greater in the case of the mandelate ion seems to lend further proof to the foregoing hypothesis.

From a study of the effects obtained, the authors come to the following general conclusion:-

> "The change in rotation of an optically active acid or of its ion produced by the cations of neutral salts is the same as that observed on passing from the active ion to the active molecule."

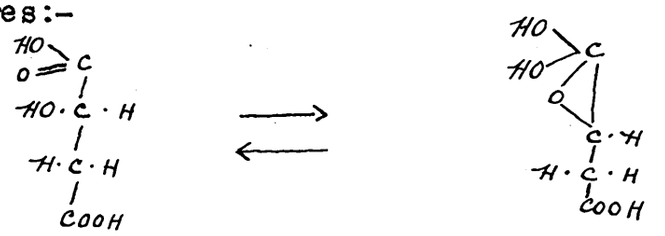
Evidence from the study of malic and tartaric acids is appended in support of the conclusion. The statement can, however, scarcely be reconciled with the work of Darmois, who found that while sodium and lithium chlorides decreased the rotation of sodium tartrate, potassium chloride acted in the opposite direction, causing an increase.

The effect of neutral salts on the rotation of α-methylglucoside and sucrose has also been

studied. The changes are very small and in the opposite direction to those obtained in the case of mandelic acid, the results being scarcely comprehensive enough to admit of the observation of regularities.

Bancroft and Davies[34.] have made an exhaustive study of the rotatory power of malic acid and various derivatives and have verified and extended much of the existing data. As has been previously mentioned, the rotatory power of *l*-malic acid changes from laevo- to dextro- as the aqueous solution is concentrated. Salts, acids and bases exert a similar influence, while rising temperature makes the solutions more laevo-rotatory.

In explanation of the above changes, the authors advance the theory that *l*-malic acid may exist in two tautomeric forms, having the following structures:-



Laevo- Dextro-

It is proposed that the d-rotatory form arises from the *l*-rotatory form when the hydrogen of the alcoholic hydroxyl group migrates to form with the ketonic oxygen of the adjacent carboxyl group a second hydroxyl group there. The resultant ethylene oxide linkage gives rise to the observed dextro-rotation of this form.

Evidence for this tautomeric change is found in the fact that when the "migrating" alcoholic hydrogen of malic acid is replaced by less labile groups, to form such compounds as methoxysuccinic acid, ethoxysuccinic acid etc., these compounds are found to possess practically constant rotation with varying aqueous concentration. Similarly, when the hydroxyl group is replaced by chlorine, chlorosuccinic acid is found to be but slightly influenced by change in concentration, while replacement of the hydrogen directly attached to the asymmetric carbon-atom by a methyl group in citramalic acid, yields rotations which vary with dilution, but to a much smaller degree than was the case with malic acid. This last the authors attribute to "the decrease in activity incident on passing from a secondary to a tertiary alcohol grouping on that carbon-atom; some migration exists, but much less than in malic acid." Finally, if the hydrogen of the alcoholic hydroxyl group is replaced by groups containing metallic atoms, such as beryllium and uranyl, the metallic derivatives show constant rotation.

The fact that numerous α-hydroxy-acids are sensitive to concentration changes, while the rotatory power of β-hydroxybutyric acid is constant under similar conditions is quoted as evidence that the migration of the alcoholic hydrogen is to the adjacent

carboxyl group and not to the more distant one.

It is also pointed out that numerous organic compounds possessing structures similar to that of malic acid undergo changes analogous to the above, phenyl azo-acetic ester and glucose being quoted.

The various theories previously advanced to account for the behaviour of malic acid are discussed at some length by the authors.

The explanation that the observed effects are due to changes in the ionisation of malic acid is criticised on various grounds. Thus the changes observed in the case of diethyl malate in absolute alcohol lead to the following statement:-

"Probably no one would claim any ionisation for ethyl malate in alcohol, and yet these data show that the rotation-dilution change is closely analogous to that of malic acid in water."

Again it is found that while dilute HCl (0.1 N) affects the rotation of dilute solutions of l-malic acid in the dextro-direction, no effect is produced in solutions more concentrated with respect to malic acid. On the other hand, stronger HCl (5 & 10 N) affects the rotation of malic acid both in the dilute and more concentrated solutions. The observed results are explained on the basis of two effects.

1. In the case of the dilute HCl, an ordinary repression of the ionisation of malic acid; the absence

of effect in the more concentrated solutions of malic acid is accounted for on the grounds that "there is practically no dissociation to be repressed."

2. In the case of the concentrated HCl, a displacement of the equilibrium in favour of the dextro-form of malic acid is supposed; the dilute HCl has no marked effect, so far as the second change is considered.

The above results are compared with those of Schneider [18], who found that the effect of sulphuric acid was about ten times as great as that of acetic acid. The authors conclude that "the ionisation theory is quite inadequate to explain such large effects."

In common with Stubbs, the conclusion is reached that neither the rotation dilution changes of malic acid, nor the effect of salts can be explained on the assumption of hydrate formation. Various pieces of evidence are quoted against this theory, among which may be mentioned "that on solution of tartaric or of malic acids, the temperature changes indicate no hydrate formation" and "the cryoscopic determinations also contradict this theory for, if hydrates form, the molecular depression of the F.P. should vary, decreasing with increase of concentration; actually it remains very constant."

The possibility that the dextro-rotatory form of *l*-malic acid is d-malic acid itself is discussed. Since, however, neither HCl nor NaOH

impart any activity to a solution of d-l malic acid, it is concluded that these substances do not favour the formation of d-malic acid from ℓ-malic acid, but that they have an equal and opposite effect on the optical antipodes.

The results obtained by the above authors are both interesting and instructive, but on one point the equilibrium theory seems weak. The ethylene oxide structure allotted to the dextro-form of malic acid is assumed to be stable in the presence of concentrated hydrochloric acid. In view of the fact tnat ethylene oxide in the presence of HCl yields ethylene chlorhydrin, the above assumption must be accepted with reserve.

From the foregoing, it is evident that many of the investigations on the optical activity of electrolytes have been carried out using hydroxy derivatives of succinic acid, e.g., malic and tartaric acids. The many abnormalities of compounds containing the hydroxyl group are well known, for example, the great variation of the rotation of malic acid with concentration and of tartaric acid with temperature.

With the above considerations in view, Campbell[35] carried out an investigation on the optical activity of ammonium-α-bromocamphor-π-sulphonate, an electrolyte containing no hydroxyl group and having a sufficiently great rotation in aqueous solution to allow of measurements in very dilute solution.

The effect of concentration and addition of salts was fully investigated. The differences in rotation were, however, very small and were in harmony neither with the original Dissociation Theory of Arrhenius nor with the "Deformation Theory" of Darmois. So far as the concentration effect is concerned, little or no variation was observed in solutions whose molar concentrations were less than 0.1.

The author concludes that "the changes observed at higher concentrations may be accounted for by assuming either changes in the degree of dissociation of the electrolyte or a deforming influence of the positive ion on the optically active negative ion."

With reference to the salt effect, it is concluded that the observed changes must be due to some factor not ionic in nature. The possibility of the existence of the ammonium salt as an equilibrium mixture of two isomers is discussed, and it is tentatively suggested that the changes observed are due essentially to a change in the equilibrium between two dynamic isomers, each of which possesses a different rotation.

The evidence outlined above yields some conception of the complexities met with in the study of optically active electrolytes. The results are in some cases conflicting, but from a general survey of the evidence, the following conclusions may be

drawn. The concentration effects and the results obtained by the addition of salts may be accounted for on the following grounds:-

1). Changes in the degree of dissociation of the optically active electrolyte.

2). The deforming influence of the cation on the optically active anion.

3). Changes in the equilibrium between two dynamic isomers, each of which possesses a different rotation.

As has been previously mentioned, most of the investigations considered have been carried out using hydroxy derivatives of succinic acid.

Part of the present investigation concerns itself with an attempt to obtain regularities with optically active electrolytes which do not contain a hydroxyl group. As parent substance, the organic acid d-sec-β-Octyl Hydrogen Phthalate was chosen, and it was decided to attempt to prepare the various salts of this acid, with a view to investigating their optical properties in aqueous and in alcohol solutions. Later the work was extended to include the effect of the addition of inorganic salts to aqueous solutions of one of the optically active salts.

Experimental.

Apparatus.

Polarimeter.

The polarimeter was a Hilger instrument, provided with a Lippich three shadow polarizer and two verniers reading to 0.01°. It was fitted with direct vision spectroscope attachments for reading rotations with the three mercury lines (yellow, green and violet). The polarimeter tubes were provided with central cap and a water-jacket, through which water was pumped from a thermostat by means of an electrically driven water turbine. The temperature of the thermostat was so regulated that the solution in the polarimeter tube was maintained at 20.0° ($\pm$ 0.2°) as measured by a special thermometer fitting the central cup.

A quartz mercury vapour lamp working at atmospheric pressure was used as source of light for the mercury green line, this line being almost exclusively used in the determination of rotations.

Solvents.

The ethyl alcohol employed in the investigation was boiled under reflux over calcium turnings and fractionated.

Chemicals.

The d-octyl alcohol and the d-sec-β-octyl hydrogen phthalate used in the following investigation

were obtained from the racemic alcohol by the method described by Pickard and Kenyon,(J.C.S., 2058, 1907, and J.C.S., 2540, 1922). The homogeneous alcohol had $[\alpha]^{20°}_{5461} = 9.6°$ in a 1 dm. tube, the rotatory power of the d-phthalate being $[\alpha]^{20°}_{5461} = 58.3°$ (in ethyl alcohol, c = 5).

Preparation of the Alkali Salts of d-sec-β-Octyl Hydrogen Phthalate.

Lithium Salt.

Two methods of preparation were employed for the production of this salt. In the first case, a methyl alcoholic solution of the d-phthalate was titrated against an aqueous solution of lithium hydroxide, using phenolphthalein as outside indicator. The resulting solution of the lithium salt was evaporated to dryness in a vacuum desiccator. The second method was precisely similar to the above, except that a methyl alcohol solution of lithium hydroxide was used in place of the aqueous solution as previously.

The purity of the salt was checked by the determination of the rotatory power of a solution prepared directly as follows:

The calculated volume of a previously standardised methyl alcohol solution of lithium hydroxide was added to a known weight of d-phthalate in methyl alcohol solution. The whole was then made up to the mark in a standard flask and the rotatory power measured.

The following were the observed rotations:-

Lithium salt by first method $[M]^{20°}_{5461}$ = 150.9° (In methyl alcohol c= 5)
" " " second " $[M]^{20°}_{5461}$ = 151.7° (" " " c=5)
" " directly prepared $[M]^{20°}_{5461}$ = 151.8° (" " " c=5)

Ammonium, Sodium and Potassium Salts.

An attempt was made to prepare the ammonium salt on similar lines to the above, using alcoholic ammonia. This method proving unsatisfactory, it was decided to prepare this salt directly in solution. In the case of the ethyl alcohol solutions, this was effected by the addition of the calculated amount of standard alcoholic ammonia to a weighed quantity of d-phthalate. In order to obtain the salt in aqueous solution, a similar method was employed, the calculated volume of standard NH_4OH being added to a weighed amount of the phthalate. The methods employed in the case of the sodium and potassium salts were exactly similar, a solution of d-phthalate in ethyl alcohol being titrated respectively against solutions of sodium and potassium ethoxide, using phenolphthalein as outside indicator. The solutions were evaporated to dryness in vacuo, and the purity of the products checked by preparation of solutions of the salts by the direct method. The rotatory powers of the sodium and potassium salts, as obtained directly in solution, compared with solutions of the solids as follows:

Sodium salt.	$[M]^{20°}_{5461}$	= 90.3°	(In ethyl alcohol c = 5).
" " (prepared directly)	$[M]^{20°}_{5461}$	= 89.3°	(" " " c = 5).
Potassium salt	$[M]^{20°}_{5461}$	= 57.3°	(" " " c = 5)
" " (prepared directly)	$[M]^{20°}_{5461}$	= 56.6°	(" " " c = 5).

Rubidium and Caesium Salts.

The mode of preparation of the rubidium salt consisted essentially of the addition of rubidium carbonate in aqueous solution to the equivalent amount of phthalate in alcohol solution. As in the previous cases, the resulting solution of the alkali salt was evaporated to dryness in vacuo. An attempt was made to prepare the caesium salt by means of silver octyl phthalate and caesium chloride, but this had to be abandoned, owing to the extreme difficulty experienced in the effort to obtain a dry product; this salt appeared to be extremely deliquescent.

Notes on the Alkali Salts.

As prepared in the manner described above, the salts were obtained as fine, white powders, all having a distinct tendency to deliquesence. Before being used, they were in all cases thoroughly dried in vacuo, and kept in desiccators during the measurement of the various rotations. To ensure that the salts remained unchanged throughout the period required for investigation, the original figure for 5% alcohol solution was repeated at the end of the series.

In some cases the solutions exhibited slight turbidity; filtration through a Jena Glass-Filter crucible was sufficient to render them perfectly clear.

Rotatory Powers of the Alkali Salts.

The rotations were all determined at approximately 20°, in aqueous and alcoholic solutions of various concentrations. The following tables give the results obtained.

d-sec-β-Octyl Lithium Phthalate. (M.W. = 284.2).

Solvent	l	M	α_{5461}	$[M]^{20°}_{5461}$
Ethyl Alcohol	4	0.035	2.26°	+160.2°
"	2	0.070	2.22°	+157.5°
"	2	0.176	5.36°	+152.2°
"	1	0.369	5.39°	+146.2°
"	1	0.528	7.53°	+142.6°
"	1	0.717	10.08°	+140.7°
Water	2	0.070	1.79°	+127.2°
"	1	0.176	0.78°	+ 44.3°
"	1	0.352	0.65°	+ 12.2°
"	1	0.530	0.00°	0.0°
"	1	0.705	-0.49°	-6.9°

In the above and following tables, l = length of polarimeter tube in decimeters, M = molar concentration of salt, α_{5461}, the observed rotation, and $[M]^{20°}_{5461}$ the molecular rotation of the solutions.

d-sec-β-Octyl Ammonium Phthalate. (M.W. = 295.2).

Solvent	l	M	α_{5461}	$[M]^{20°}_{5461}$
Ethyl alcohol	4	0.036	2.13°	147.5°
"	2	0.072	2.01°	139.7°
"	1	0.183	2.40°	131.3°
"	1	0.360	4.57°	126.9°
"	1	0.539	6.61°	122.7°
"	1	0.719	8.57°	119.2°
"	1	1.078	11.95°	110.9°
Water	2	0.072	1.58°	109.7°
"	1	0.180	0.60°	33.3°
"	1	0.360	0.20°	5.6°
"	1	0.540	-0.36°	-6.7°
"	1	0.899	-1.74°	-19.4°

d-sec-β-Octyl Sodium Phthalate.* (M.W. 300.3).

Solvent	l	M	α_{5461}	$[M]^{20°}_{5461}$
Ethyl Alcohol	4	0.034	1.55°	115.1°
"	2	0.067	1.45°	107.7°
"	1	0.168	1.52°	90.3°
"	1	0.335	2.44°	72.7°
"	1	0.500	2.99°	59.8°
"	1	0.666	3.37°	52.1°
"	1	0.833	3.68°	44.2°
Water	2	0.067	1.62°	120.3°
"	1	0.169	0.79°	46.8°
"	1	0.335	0.21°	6.3°
"	1	0.502	-0.56°	-11.2°
"	1	0.668	-1.33°	-19.9°
"	1	0.833	-2.08°	-25.0°

*This salt was previously examined by McGillivray, (Rule, Miles and McGillivray, J.C.S., 2274, 1929), who found that the rotations of the alcohol solutions showed a minimum at c = ca 18 (0.6 M). A careful repetition of the results (above table) failed to establish the existence of such a minimum.

d-sec-β-Octyl Potassium Phthalate (M.W. 316.4).

Solvent	l	M	α_{5461}	$[M]^{20°}_{5461}$	
Ethyl Alcohol	4	0.032	0.94°	74.2°	
"	2	0.063	0.85°	67.3°	
"	2	0.165	1.85°	57.3°	
"	1	0.331	1.55°	48.4°	
"	1	0.475	1.98°	41.6°	
"	1	0.640	2.36°	36.9°	
Water	2	0.064	1.58°	122.6°	
"	1	0.167	0.62°	37.2°	
"	1	0.316	-0.22°	-7.0°	
"	1	0.474	-1.10°	-23.2°	
"	1	0.666	-2.45°	-36.8°	

d-sec-β-Octyl Rubidium Phthalate (M.W. 362.8)

Only a small quantity of this salt was prepared; the rotations were determined in alcohol solution.

Solvent	l	M	α_{5461}	$[M]^{20°}_{5461}$	
Ethyl Alcohol	4	0.028	0.73°	65.4°	
"	2	0.055	0.65°	58.8°	
"	1	0.139	0.67°	48.0°	
"	1	0.276	1.14°	41.3°	
"	1	0.413	1.61°	38.9°	
"	1	0.551	1.99°	36.1°	

d-sec-β-Octyl Hydrogen Phthalate.*

Solvent	M	$[M]_{5461}$
Ethyl Alcohol	0.180	162.0°
"	0.719	159.0°
"	1.078	156.7°

* Rule, Hay, Numbers and Paterson, J.C.S., 178, 1928. The values were quoted as $[M]_{5893}$; these were converted by use of the ratio $\frac{[M]_{5461}}{[M]_{5893}} = 1.21$, giving the above figures.

Addition of Inorganic Salts.

d-sec-β-octyl sodium phthalate in 0.2 M aqueous solution was employed throughout as optically active solute.

In most cases the salts used were the purest obtainable - "A.R." products being employed. When these were not available, the ordinary quality of salt was used, after recrystallisation from water. Whenever possible, the solutions were made up by direct weighing. Deliquesent salts however (e.g. $CaCl_2$ and $MgCl_2$) render such a method impracticable; salts of this type were therefore added in solution, the strength of which had been previously determined by analysis. It was originally intended to work throughout with the following concentrations; inorganic salt 0.5 M, d-sec-β-octyl sodium phthalate 0.2 M. In the case of some of the divalent salts, however, (e.g. Ca, Sr, Ba salts), the solubility of the Ca, Sr, Ba phthalates was so extremely small that concentrations of inorganic salt much lower than 0.5 M were necessitated.

The rotatory power of the d-sec-β-octyl sodium phthalate was determined in aqueous solution before and after the investigation, thus ensuring that it had undergone no change.

The results are summarised in the following tables:

Addition of Alkali Chlorides (0.5 M) to Aqueous Solutions of d-sec-β-Octyl Sodium Phthalate. (0.2 M).

Salt added	l	α_{5461}	$[\alpha]^{20°}_{5461}$	Δ
-	2	+1.35°	11.24°	-
LiCl	"	-0.04°	-0.33°	-11.57°
NH_4Cl	"	-0.19°	- 1.58°	-12.82°
NaCl	"	-0.58°	-4.83°	-16.07°
KCl	"	-1.06°	-8.82°	-20.06°
RbCl	"	-1.31°	-10.90°	-22.14°
CsCl	"	-1.79°	-14.90°	-26.14°

Δ = difference in specific rotation observed.

Addition of Divalent Salts to Aqueous Solutions of d-sec-β-Octyl Sodium Phthalate. (0.2 M).

Salt added	l	M	α_{5461}	$[\alpha]^{20°}_{5461}$	Δ
-	2	-	+1.36°	11.32°	-
$CaCl_2$	"	0.025	+0.66°	5.50°	-5.82°
$CaCl_2$	"	0.0375	+0.47°	3.91°	-7.41°
$SrCl_2$	"	0.025	+0.56°	4.66°	-6.66°
$SrCl_2$	"	0.0375	+0.37°	3.08°	-8.24°
$BaCl_2$	"	0.0125	+0.92°	7.66°	-3.66°
$BaCl_2$	"	0.025	+0.54°	4.50°	-6.82°
$BaCl_2$	"	0.0375	+0.31°	2.58°	-8.74°
$BaCl_2$	"	0.05	+0.13°	1.08°	-10.24°
$MgCl_2$	"	0.0375	+0.59°	4.91°	-6.41°
$MgCl_2$	"	0.05	+0.38°	3.16°	-8.16°
$MgSO_4$	"	0.05	+0.32°	2.66°	-8.66°
CsCl	"	0.05	+0.51°	4.25°	-7.07°
KCl	"	0.05	+0.78°	6.49°	-4.83°
KCl	"	0.10	+0.38°	3.16°	-8.16°

Δ has the same significance as before; M = molarity of added salt.

The results for KCl and CsCl are included in the above table for purposes of comparison.

The addition of the chlorides of mercury and cadmium proved to be a matter of some difficulty, the octyl phthalates of these metals being practically insoluble in water. It was, however, found that the addition of alcohol to the aqueous solution had the effect of dissolving the precipitated salts. The investigation of the addition of the above chlorides was therefore carried out in aqueous alcohol, (50/50 by volume). The results obtained are given below.

Addition of Chlorides to Aqueous-Alcohol Solutions of d-sec-β-Octyl Sodium Phtnalate (0.2 M).

Salt added.	l	M	α_{5461}	$[\alpha]^{20°}_{5461}$	$\triangle$
-	2	-	5.37°	44.7°	-
$HgCl_2$	"	0.025	5.31°	44.2°	-0.5°
$CdCl_2$	"	0.025	5.10°	42.5°	-2.2°
CsCl	"	0.05	4.78°	39.8°	-4.9°

M and $\triangle$ have the same significance as before.

Discussion of Results.

Before entering into a detailed consideration of the observed effects, one particular aspect of the problem will be briefly discussed, namely, the case of aqueous solutions of the salts under investigation. The organic acid d-sec-β-octyl hydrogen phthalate being a weak acid, it may be regarded as very probable that its salts will be hydrolysed to a considerable extent in aqueous solution.

With this consideration in view, the rotatory power of the sodium salt was determined in aqueous solution and in N/20 sodium hydroxide solution. In addition, similar determinations were made in ethyl alcohol solution and in N/20 sodium ethoxide solution. The results are briefly summarised below:-

Solvent	l	c	α_{5461}	$[M]^{20°}_{5461}$
Water	1	5.070	0.79°	46.8°
N/20 NaOH	"	5.060	0.58°	34.4°
Ethyl alcohol	"	5.030	1.51°	90.2°
N/20 NaOEt	"	5.028	1.49°	89.0°

Thus the rotatory power of the sodium salt in dilute sodium hydroxide solution is appreciably lower than in aqueous solution. On the other hand, the observed difference in the case of ethyl alcohol

and dilute sodium ethoxide is not much greater than the experimental error in reading the polarimeter and hence is practically negligible. It would therefore appear that while the sodium salt undergoes considerable hydrolysis in aqueous solution, there is no evidence for any appreciable chemical change in alcohol solution. Aqueous hydrolysis, as was to be expected, results in an abnormally high rotatory power in the more dilute solutions, the mechanism of the reaction being illustrated by the following equation:-

$$H_2O + R.COONa \rightleftarrows R.COOH + NaOH$$

Since the rotation of the free acid is greater than that of the sodium salt, (p. 48.), the effect of hydrolysis must be to cause an increase in the rotatory power of the solution as a whole.

It must be pointed out, however, that the diminution in rotation observed upon addition of NaOH and NaOEt may in part be attributed to the influence of the added sodium ions. (see p. 52.).

Variation of the Rotatory Power with Concentration.

Salts of d-sec-β-Octyl Hydrogen Phthalate.

Ethyl Alcohol Solutions.

In alcohol solution the rotations of all the salts examined underwent definite changes with concentration, decreasing with increasing concentration. (See graphs p. 50.). As was concluded in the Introduction, similar variations (e.g. in the case of the tartrates and malates) have been adequately explained on the grounds of changes in the degree of ionisation of the electrolyte and the deforming influence of the cation on the optically active anion.

By plotting the various curves on a single graph, a significant regularity is observed. For convenience the rotatory powers of the various salts in 0.2 M alcohol solution are summarised below.

Rotatory Power in 0.2 M Ethyl Alcohol Solution.*

Acid or Salt	M	$[M]^{20°}_{5461}$
Acid	0.2	162°
Lithium	"	151°
Ammonium	"	131°
Sodium	"	87°
Potassium	"	55°
Rubidium	"	45°

* A. McLean, working in these laboratories, has obtained the following results for alkali salts of ℓ-menthyl hydrogen naphthalate in methyl alcohol.

Rotatory powers of 5% solutions of ℓ-Menthyl Hydrogen Naphthalate and Alkali Salts.

Acid or Salt	$[M]^{20°}_{5461}$
Acid	-215.9°
Lithium	+ 0,67°
Sodium	+ 4.25°
Potassium	+ 11.93°

Aqueous Solutions.

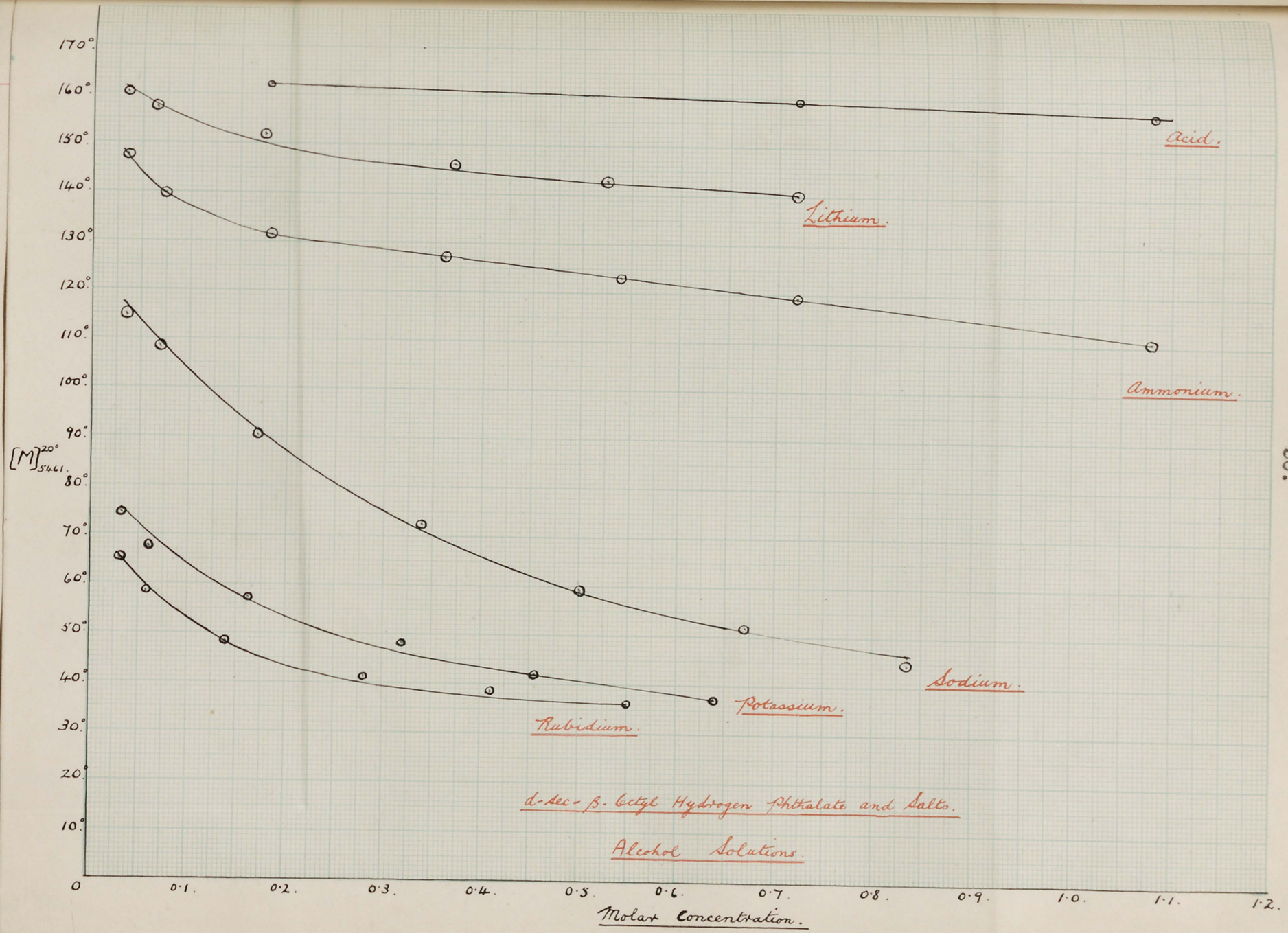
In dilute aqueous solutions the changes in rotation with concentration are considerably greater than those observed in the alcohol solutions. It appears probable, however, that the magnitude of the variations may be accounted for, in part, by the fact that the salts undergo hydrolysis in aqueous solution, an aspect of the question which has already been discussed.

As was the case in alcohol solutions, the rotatory power decreases with increasing concentration, but with this solvent the original dextro-rotation passes through inactivity, becoming a laevo-rotation in the more concentrated solutions. Moreover, in the last mentioned solutions a regularity is obtained, precisely similar in nature to that observed with alcohol as solvent. The following table contains the observed rotations for the various salts in 0.5 M aqueous solution.

Rotatory Powers in 0.5 M Aqueous Solution.

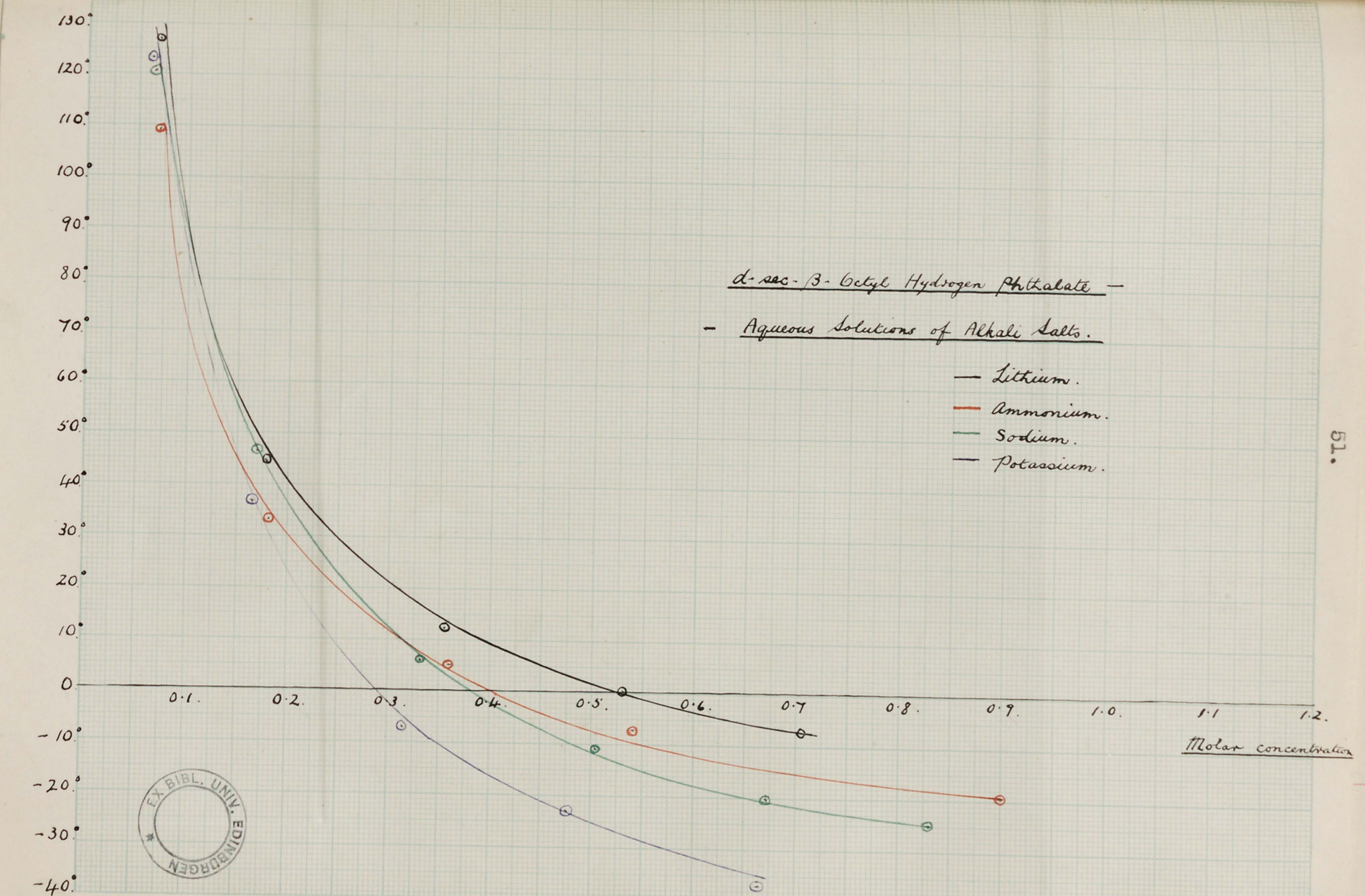
Salt	M	$[M]^{20^\circ}_{5461}$
Lithium	0.5	+1.5°
Ammonium	"	-5.5°
Sodium	"	-11.0°
Potassium	"	-27.0°

In the above table and in that quoted previously for alcohol solutions, the values of $[M]^{20^\circ}_{5461}$ are obtained



d-sec-β-Octyl Hydrogen Phthalate and Salts.

Alcohol Solutions.



graphically. (See Graphs pp.50 & 51).

It may be fairly assumed that, in alcohol solution, the degree of ionisation of the various salts will be considerable. From the view-point that the observed effects may be attributed to ionic influence, a study of the tabulated rotatory powers of the salts in alcohol solution reveals the following series, in which the ions are arranged in order of depressive effect:-

$$Rb^+ > K^+ > Na^+ > NH_4^+ > Li^+ > (H)$$

The results quoted above for the salts in aqueous solution show that an order of influence of the ions exactly similar to the foregoing is obtained.

The parallelism between the above effects and those obtained by Darmois[30] in the case of the alkali tartrates is unmistakable. Compared with the free acid, all the tartrates studied show an increased rotation, lithium producing the least effect and rubidium the greatest. As we have seen, Darmois explains his results on the basis of two influences, a "deformation effect" and a "dehydration effect", the latter involving the assumption that the tartrate ion is hydrated in solution. This dehydration theory has been rejected by other authors, but little evidence has been brought forward negative to the assumption of hydration. Bancroft and Davies[34] have, however, pointed out that the temperature changes observed on solution of tartaric acid indicate no

hydrate formation.

In the case of the alkali and ammonium octyl phthalates, it would appear that the observed effects on the rotatory power may be attributed to a deformation of the optically active anion produced by the electric field of the cation; also that the solvation of the cation must be taken into account.

The general problem of solvation is much too complicated to be entered into in detail here, but the extent of our present knowledge of the subject may be briefly summarised in the following statements, due to Sidgwick.[36]

"We cannot.... determine the degree of hydration in solution, and we commonly assume that if a solid hydrate of a particular formula separates, this hydrate also exists as a molecule (or as the ions of a molecule) in solution."

"The hydration of ions in solution has been investigated by means of a great variety of physical properties ..... The experimental evidence is thus extensive enough, but it is very indecisive." Finally, the conclusion is reached that "there is good reason to believe that many ions are hydrated in water, and some evidence as to which ions are more hydrated and which less, but we can form no quantitative idea of the number of water molecules combined in solution with any particular ion."

Of importance with regard to the above

problem is the fact that a water molecule can be co-ordinated to another atom in two ways - either by the oxygen of the water acting as a donor, or by the hydrogen acting as an acceptor. While it is recognised that there is a possibility of the hydration of both cations and anions, it is generally concluded, from the fact of the greater co-ordinating power of the oxygen in water, that the cations will hydrate more easily than the anions.

A particular aspect of the subject of hydration now falls to be dealt with, namely, the hydration of cations.

In accordance with Fajans' theory, this hydration increases with the electrovalency, being weak with univalent metals, stronger with divalent and stronger still with trivalent. A consideration of some moment with respect to the present work is that in any given periodic group the tendency to hydration is strongest in the lightest members, diminishing as the atomic number increases.

Thus, with the exception of lithium and sodium, all the univalent metals (e.g., K, Rb, Cs) are almost invariably anhydrous in their salts, and lithium salts are more uniformly and on the average more highly hydrated than those of sodium.

A study of the rotation values previously quoted for the alkali salts of d-sec- β-octyl hydrogen phthalate in alcoholic and aqueous solutions

reveals the interesting fact that a definite connection can be traced between the degree of hydration of the cations and their effect on the rotatory power. Assuming that the observed differences in rotatory power may be traced in part to a modification of the optically active anion under the influence of the cation, it is seen that the most highly hydrated ion (Li^+) exerts least effect, while the Rb^+ ion, for which we suppose least hydration , has the greatest influence.

A second possibility must, however, be admitted, it being unlikely that the rotatory powers of the undissociated acid and undissociated salts are identical. Since the degree of ionisation of the salts is probably great at the concentrations considered, this second effect, whatever its nature, would appear to be a minor one.

From the above point of view, an interesting study is afforded by the values quoted by Darmois for the radii of the alkali cations in aqueous solution; these radii, calculated from ionic mobility with the aid of Stokes' formula, are given as follows:

Li	Na	K	Rb	Cs	
2.30	1.79	1.22	1.17	1.17	Å.

If the modification of the optically active anion is assumed to be produced by the electric field of the cation, then the effect should reach a

maximum in the case of Rb and Cs.

As we have seen, experimental evidence affords confirmation of this view, the greatest influence being observed in the case of rubidium, while the observed effects in the case of the remaining metals are in the order of the ionic radii quoted above.

Addition of Salts.

We shall first consider the effects obtained by the addition of the alkali chlorides to aqueous solutions of d-sec-β-octyl sodium phthalate.

The results are briefly summarised below:-

Addition of Alkali Chlorides (0.5 M) to Aqueous Solutions of d-sec-β-Octyl Sodium Phthalate.(0.2 M).

Salt added	△
LiCl	-11.6°
NH_4Cl	-12.8°
NaCl	-16.1°
KCl	-20.1°
RbCl	-22.1°
CsCl	-26.1°

△ is the observed difference in specific rotation..

Since a comparison with the previously quoted rotatory powers for solutions of the salts was desired, the series was completed by a determination of the depressive influence of NH_4Cl.

The addition of inorganic chlorides to the sodium salt of d-sec-β-octyl hydrogen phthalate, as above, leads to results precisely similar to those observed in the case of solutions of the alkali salts of the active acid.

From a study of the relative influences of

the various cations, a series identical with that for the alkali and ammonium octyl phthalates may be deduced; Li^+ again has least effect, the maximum being reached in the case of Cs^+.

In order to gain further information with regard to the cation influence, the effect of addition of a series of divalent salts to aqueous solutions of d-sec-β-octyl sodium phthalate was investigated. If, as has been postulated, the cation influence can be traced to the electric field of the cation, then we should expect divalent salts, in general, to exert a greater depressive effect than monovalent salts. The extent to which this is borne out in practice can be seen from the following results.

Addition of Monovalent and Divalent Salts to Aqueous Solutions of d-sec-β-Octyl Sodium Phthalate. (0.2 M).

M is the molarity of the added salt, Δ having the same significance as before.

Salt added	M	Δ
$CaCl_2$	0.0375	-7.41°
$SrCl_2$	"	-8.24°
$BaCl_2$	"	-8.74°
$BaCl_2$	0.05	-10.24°
$MgCl_2$	0.0375	-6.41°
$MgCl_2$	0.05	-8.16°
$MgSO_4$	0.05	-8.66°
CsCl	0.05	-7.07°
KCl	"	-4.83°
KCl	0.10	-8.16°

The experimental evidence is thus in harmony with the original postulate, all the divalent salts examined exerting a greater influence than does CsCl, which produced the maximum effect in the case of the monovalent salts, comparison being made under similar conditions as to concentration.

Generally speaking, the results are strikingly similar to those obtained by Stubbs,[27] who investigated the effect of addition of inorganic salts

to aqueous solutions of l-malic acid. (See introduction p.12). They are also in harmony with the work of Patterson and Anderson[29] on aqueous solutions of ethyl tartrate. (See p.16.).

A study of the tabulated values of $\triangle$ for the monovalent salts shows that the order of influence of the cations is as follows:-

$$Cs^+ > Rb^+ > K^+ > Na^+ > NH_4^+ > Li^+$$

The above series, even to the position of NH_4^+, is identical with that quoted by Stubbs for l-malic acid.

This agreement as to the position of NH_4^+ is a point of some interest, Darmois finding, in the case of the tartrates, that NH_4^+ exerts a greater influence than does Na^+.

A comparison of the present writer's results for addition of divalent salts with those of Stubbs makes an interesting study.

Thus the last-mentioned author, whose investigation was somewhat extensive, deduces the following series for the cation effect:-

$$Ba^{++} > Ca^{++} > Cd^{++} > Mg^{++} > Al^{+++} > Zn^{++} > Hg^{++}$$

The order of cationic influence for the addition of divalent salts to aqueous solutions of d-sec-β-octyl sodium phthalate is

$$Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} \quad (> Hg^{++}).$$

As will be seen later, $HgCl_2$ is found to exert a

remarkably small effect, so that the results are again in agreement with those of Stubbs.

This author's conclusion that "the influence is mainly a specific additive property of the ions or radicles and appears to be related with the valency of the ions and their order of electro-affinities" is essentially the same as the view taken by the present writer , differing only inasmuch as in the present case account has been taken of the ionic radii, this latter involving a consideration of ionic hydration.

As was stated in the experimental section, (p.45) some difficulty was experienced in examining the addition of the chlorides of mercury and cadmium to aqueous solutions of d-sec-β-octyl sodium phthalate, and the determinations were finally carried out in aqueous alcohol.

Addition of Chlorides to Aqueous-Alcohol Solutions of d-sec-β-Octyl Sodium Phthalate (0.2 M).

M and Δ have the same significance as before.

Salt added	M	Δ
$HgCl_2$	0.025	-0.5°
$CdCl_2$	0.025	-2.2°
CsCl	0.05	-4.9°

The value for CsCl is included for purposes of comparison.

The case of mercuric chloride is a very interesting one. Mercury occupies a unique position among the metals, the mercuric compounds, with few exceptions, ionizing only to a very small extent. Mercuric chloride being only very slightly ionised, we should expect its influence on the rotatory power of an optically active solute to be small. That this is actually the case in practice seems to lend further confirmation to the view that the observed effects are ionic in nature.

It has been suggested that the concentration effects may, in part, be attributed to changes in the degree of ionisation of the optically active electrolyte. Some information as to the relative importance of this effect may be obtained by a consideration of the added salt influence.

We shall consider the general case, the optically active salt and the added salt having no common ion. In this case the equilibrium seems to be governed by the "total ion concentration", i.e. the sum of the concentrations of all the positive or negative ions.

In a solution containing NaCl and K_2SO_4, $2\,NaCl + K_2SO_4 \rightleftarrows 2KCl + Na_2SO_4$, Sherril[37], for example, found that the equilibrium is governed by $[Na^+] + [K^+]$.

Consider now the case of an aqueous solution of d-sec-β-octyl sodium phthalate (0.2 M) to which an

inorganic salt (0.05 M) has been added. Since the optically active salt is in considerable excess, the change in the degree of ionisation of this salt is probably small. The fact that the observed change in the rotatory power is considerable appears to indicate that some other factor, of more moment than the mere ionisation change, must be taken into account.

Again, on the Arrhenius Theory, the ionisation of salts is determined to a large extent by the salt type - uni-univalent, uni-divalent etc.

Degree of Dissociation of 0.5 N Solutions of Several Electrolytes.

Determined by conductivity measurements.

Salt	Degree of Dissociation
KCl	78%
$BaCl_2$	67%
$MgSO_4$	38%

The order of the degree of dissociation of the above salts is $KCl > BaCl_2 > MgSO_4$.

If then the observed changes in the rotatory power are mainly due to variations in the degree of disscciation of the optically active salt, then addition of the above inorganic salts, in comparable concentrations, should lead to influences, the magnitudes of which should be in the same order as the

several degrees of dissociation.

This was not found to be the case.

Rotatory Power of d-sec-β-Octyl Sodium Phthalate (0.2 M Aqueous solution) in presence of Different Salt Types (0.05 M).

Salt added	△
KCl	-4.83°
$BaCl_2$	-10.24°
MgSO4	-8.66°

A comparison of the effects of the above salts in 0.1 N aqueous solution shows that the order given remains unaltered, △ for KCl in this case being -8.16°.

Since, however, it has been established that the conductivity ratio $\frac{\lambda c}{\lambda \infty}$ does not yield an accurate measurement of the degree of dissociation of an electrolyte, the above method of treating such solutions is open to criticism. Indeed the possibility of examining quantitatively equilibria between ions and undissociated molecules has been questioned.[38.]

In view of such difficulties, the general problem of solutions of electrolytes has been studied from a thermodynamical viewpoint. Thus G. N. Lewis, from a study of free energy changes has defined a new

quantity, the activity of an electrolyte or ion, from which is derived the activity coefficient or thermodynamic degree of dissociation.

$$\text{Activity coefficient of electrolyte} = \frac{\text{Mean Activity of the Ions.}}{\text{Molality of the Electrolyte.}}$$

This quantity affords a measure of the fraction of the concentration of the electrolyte which is active from the chemical point of view.

In formulae, therefore, the activity or the product of molal concentration and the thermodynamic degree of dissociation is used in place of molar concentration.

As we have seen, the degree of dissociation, as determined by conductivity measurements, is conditioned by the type of electrolyte. Lewis and Randall[39] have shown that a similar state of affairs exists in the case of thermodynamic degree of dissociation.

It is of interest, therefore, to ascertain whether or no any relationship exists between the activities of salts and their effect on rotatory power.

Activity Coefficients of Several Electrolytes.[40]

KCl	0.840
$BaCl_2$	0.568
$MgSO_4$	0.225

Molality = 0.05.

As was the case with the degrees of dissociation determined by conductivity measurements, the activity coefficients of the salts and their effects on the rotation of aqueous solutions of d-sec-β-octyl sodium phthalate would not appear to be related.

Another interesting study is afforded by a consideration of a new concept introduced by Lewis and Randall,[41] namely, the ionic strength of a solution. The ionic strength of a solution of electrolytes is defined as half the sum of the molality of each ion multiplied by the square of its valence, i.e. $\mu = \sum \frac{mz^2}{2}$, where μ is the ionic strength, m the molality, and z the valence of each different ion in the solution.

Consider the case of aqueous solutions of d-sec-β-octyl sodium phthalate (0.2 M) containing salts of different valence types, (0.05 M). The ionic strengths being different, the question may be asked - is there any relationship between the effect of added salts on the optical activity of an electrolyte and the ionic strength of the solution?

The following results would appear to indicate that, at the concentrations considered, no simple relation exists.

Rotatory Power of d-sec-β-Octyl Sodium Phthalate (0.2 M Aqueous Solution) in presence of Different Salt Types. (0.05 M)

Salt added	μ	Δ
KCl	0.25	-4.83°
$BaCl_2$	0.35	-10.24°
$MgSO_4$	0.40	-8.66°

μ = ionic strength.

It would therefore seem that any explanation of the observed effects must involve a consideration of the specific effect of the ions, which idea is in harmony with our previous conclusions.

As was stated in the Introduction, most of the previous investigations on the effect of addition of salts on optically active electrolytes have been carried out using as optically active solutes compounds containing the hydroxyl group.

A notable exception is found in the case of Campbell's[35] work on ammonium.α.bromocamphor.π. sulphonate. The changes in rotatory power, were, however, very small and practically no regularities were observed. In this connection the above author considers a statement of Walden's,[42] who suggested that the structure of the camphor molecule may render the asymmetric carbon atoms less sensitive to changes in ionisation or to the influence of the cation.

Of considerable interest with regard to this problem is a finding due to Darmois[43]. "..... the rotatory power of camphor in alcohol is not influenced by the addition of KI, so that in this case, the effect of the salt is null, in spite of its electrolytic dissociation."

Campbell also suggests that the large changes observed in the case of the salts of the hydroxy acids may be due to the presence of the OH group and that electrolytes containing no groups possessing residual affinity (other than the $-SO_3H$ or -COOH group) do not exhibit great changes in rotation.

In the light of the present writer's results, obtained by use of an optically active electrolyte containing a -COOH but no -OH group, the above suggestion would not appear to be valid..

Summary.

1. The rotatory powers of the alkali and ammonium salts of d-sec-βoctyl hydrogen phthalate have been studied in alcoholic and aqueous solution. The rotations of the salts were found to be in the order

$$H > Li > NH_4 > Na > K > Rb.$$

2. It has been concluded that the variation of the molecular rotation of the salts with concentration may be explained by assuming changes in the degree of dissociation of the electrolytes and a deforming influence of the cations on the optically active anions.

3. The effect of the addition of inorganic salts of various valence types to 0.2 M aqueous solutions of d-sec-β-octyl sodium phthalate has been investigated.

The series for the depressive influence of the alkali and ammonium chlorides on the rotatory power of the optically active electrolyte is

$$Cs^+ > Rb^+ > K^+ > Na^+ > NH_4^+ > Li^+.$$

The corresponding series for the divalent chlorides is

$$Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++}.$$

It is concluded that the observed effects may be attributed mainly to a deforming influence of the

positive ion on the optically active negative ion, the explanation involving a consideration of the ionic radii.

4. It is worthy of comment that the above results have been obtained by use of a carboxylic acid containing no hydroxyl group.

Solvent Effect.

Introduction.

Although the influence of solvents on the rotatory power of optically active solutes has been much studied in recent years, much more work remains to be done before its nature will be made generally clear.

In view of the comparatively subsidiary nature of the investigation of solvent effect in the present communication, the following discussion is confined to a brief summary of a few recent and typical researches on the above subject.

Thus Pickard and Kenyon[1] have examined the rotatory powers of a number of esters of the general formula $CH_3.CHX.O.CO.R$ where R is the optically active radical and X is C_2H_5, C_3H_7, C_4H_9 etc. The rotations of most of the esters were determined in various solvents, and it was found that the rotatory powers of β-butyl acetate, β-octyl acetate, heptoate and stearate respectively were influenced similarly by the following solvents: Ethylene dibromide, acetone, ethyl acetate, ethyl alcohol, chloroform, benzene and carbon disulphide.

A comparison of the values of $[\alpha]_D^{20^\circ}$ for the esters in the homogeneous state with those obtained in various 5% solutions at 20°, shows that the

various solvents depress the specific rotatory power. It is interesting to note that the depression caused by ethyl alcohol, benzene, pyridine and carbon disulphide is in the order $C_2H_5OH < C_6H_6 < C_5H_5N < CS_2$, inasmuch as this series holds for almost every ester examined; the depression in the case of carbon disulphide was in most cases sufficient to cause a reversal of sign.

From a general consideration of the results, the authors conclude that the solvent effect would appear to be due to "an alteration in the degree of association or complexity of the molecules of the optically active compounds."

Rule and Mitchell[2] have made a thorough investigation of the rotation of several d-β-octyl esters of monosubstituted acetic acids in the homogeneous state and in various solvents. The following is a short summary of the results obtained.

Molecular Rotations, $[M]_D^{20°}$, of d-β-octyl Esters in Various 5% Solutions.

Solvent	Acetate	Methoxy-acetate	Chloro-acetate	Bromo-acetate	Iodo-Acetate.
Ethylene dibromide	+16.8°	+19.2°	+21.3°	+30.3°	+41.1°
(Homogeneous ester)	11.8°	16.3°	17.9°	28.8°	43.7°
Acetone	9.6°	11.9°	13.2°	25.2°	45.3°
Nitromethane	9.0°	12.4°	14.1°	23.8°	41.9°
Ethyl acetate	8.9°	12.5°	14.9°	26.5°	45.1°
Chloroform	6.5°	11.6°	12.6°	22.7°	38.3°
Acetic acid	6.3°	11.6°	11.5°	25.9°	43.0°
Ethyl alcohol	6.1°	11.3°	12.9°	26.4°	46.8°
Carbon tetrachloride	6.0°	13.0°	16.4°	28.0°	41.4°
Toluene	-	0.8°	-	10.8°	-
Benzene	-1.4°	-1.0°	0.8°	10.1°	18.9°
Phenetole	-2.4°	-6.4°	-5.2°	4.9°	16.4°
Chlorobenzene	-5.3°	-7.1°	-6.7°	2.5°	12.1°
Bromobenzene	-	-7.0°	-8.8°	1.6°	9.1°
Iodobenzene	-	-12.7°	-9.9°	-1.0°	2.9°
Carbon disulphide	-15.4°	-14.7°	-10.7°	-1.2°	7.1°

The values for the acetate in the above table are those quoted by Pickard and Kenyon.[1.]

In order to determine the relative effects of different substituents the values of $[M]_D^{20°}$ for the homogeneous esters are compared with those recorded by Pickard and Kenyon.

Substituent.	H.	Me.	OMe.	Et.	Cl.	Br.	I.
$[M]_D^{20°}$	+11.8°	13.0°	16.3°	17.9°	17.9°	28.8°	43.7°

Substituent influence in the octyl acetates is therefore represented by the series

$$I > Br > Cl > C_2H_5 > OCH_3 > CH_3 > H.$$

As may be seen from the above table, the presence of solvents affects each of the esters in approximately the same manner, the result in most cases being a decrease in rotation and not infrequently a reversal of sign. With a few exceptions, it is found that the order of the rotatory powers of the five esters in any given solvent is the same as that of the esters in the homogeneous state.

The authors remark that "it is significant that the substituent having the most pronounced effect on the rotatory power of the parent ester should also bring about the most specific changes in the behaviour of the substituted esters towards solvents."

A survey of the various regularities obtained leads to the conclusion that the solvent influence would appear to be exerted through the medium of the carboxyl group.

By the use as solvents of benzene

and its substituted derivatives, of general formula C_6H_5X, a very interesting regularity emerges. The depression of the rotatory power of a given ester, due to the variation of X in the solvent molecule, is expressed by the series

$$I > Br > Cl > OC_2H_5 > H > CH_3.$$

This series holds for each of the esters and is almost the exact reverse of that representing the effect of the substituents when introduced into the optically active molecule.

To quote H. G. Rule[3] on this point; "the coincidence can hardly be fortuitous and each set of changes is probably related to the dipole moments due to the substituent groups. The emergence of this striking relationship between substituent effect in the solvent and in the asymmetric molecule is evidently dependent on the very close structural similarity of the solvents employed."

The rotatory powers of a number of *l*-menthyl esters of substituted naphthoic acids have been determined by Rule, Spence and Bretscher.[4] In the main, the investigations were concerned with the effect of substituents in the active molecule, but several of the esters were examined in different solvents. In particular, *l*-menthyl 2-methoxy-1-naphthoate was examined in various solvent types and to a lesser degree, the variations in the case of *l*-menthyl 1-naphthoate and *l*-menthyl 8-methoxy-1-

naphthoate were also observed. The following is a brief summary of the results obtained.

l-Menthyl 2-Methoxy-1-naphthoate.

Solvent	Concentration (gm/100 c.c.)	$[M]^{20^\circ}_{5461}$
Benzene	5	+28.9°
"	20	+45.3°
Carbon disulphide	5	-16.3°
" "	34	+20.6°
Acetone	5	-62.2°
Chloroform	5	-76.2°
"	30	-48.0°
"	40	-39.9°

l-Menthyl 1-naphthoate.

Solvent	c	$[M]^{20^\circ}_{5893}$
Ethyl alcohol	8.991	-247°
Benzene	4.938	-273°
Chloroform	4.990	-222°

l-Menthyl 8-Methoxy-1-naphthoate.

Solvent	c	$[M]^{20^\circ}_{5461}$
Ethyl alcohol	5.000	-184.5°
Benzene	4.987	-157°
Carbon disulphide	4.972	-137.5°

The above tables show that the rotatory powers of the esters undergo considerable variation with change of solvent, the sign being reversed in some cases. The changes are discussed mainly from

the viewpoint of substituent effect, the authors remarking that "the substituent influence ..... tends to be exerted to the maximum extent in solvents of low dielectric constant....."

Of great interest with regard to the general problem of polarity is a discussion published in 1923 by Sir J. J. Thomson.[5] In an attempt to explain orientation effects in benzene substitution, this author compared the introduction of a polar group into a hydrocarbon molecule to the insertion of an electrostatic doublet. The introduction of such doublets was shown to impart an electric moment to the molecule; this, in turn, to affect the specific inductive capacity of the compound. Further, the statement was made that a determination of the relative magnitude of these electrostatic doublets, irrespective of sign, could be made by a comparison of the molecular inductive capacities for long wavelengths, of organic compounds of the type RX, where R is the hydrocarbon radical and X the variable substituent.

Thomson also proposed that the magnitude in question is a vector quantity. Thus, in di-substituted benzenes, the effect of two similar substituents in ortho-position would be to reinforce one another, while in para-position the effect would be one of neutralisation; for dissimilar doublets the reverse state of affairs is supposed.

Within recent years a number of investigators have concerned themselves with the determination of dipole moments of compounds. The dipole moment of a hydrocarbon molecule may be defined as follows. The electrical centres of the electrons and nuclei in a molecule do not, in general, coincide. The distance between the resultant poles, multiplied by the charge on one of them is termed the dipole moment, a quantity which may be calculated from data referring to the dielectric constant and refractivity of the compound, by methods suggested as early as 1912, by Debye.[6.] Research by C. P. Smyth;[7.] J. W. Williams,[8.] K. Höjendahl;[9.] J. Errera[10.] and others on dipole moment leads to the assumption that this quantity is a characteristic of the substituent polar groups, and largely independent of the hydrocarbon radicals to which they are attached. It has further been concluded that substituents may be divided into two classes identical with the older arrangement into electronegative and electropositive groups, namely,

1) NO_2, OH, COOH, Cl, Br, I and OCH_3

and 2) CH_3, NH_2 and $N(CH_3)_2$.

This classification of groups replaces that originally proposed by Sir J. J. Thomson. From the values for dipole moment assigned to the various substituents, it is possible to deduce a series ranging from strongly electronegative groups to those of strongly electropositive character, neutral hydrogen being intermediate.

Of such a nature is the following order of substituents:

NO_2, CN, Halogens, OCH_3, H, CH_3, $N(CH_3)_2$, NH_2.

Of immediate interest here is the action of solvents containing the above type of substituent on an optically active solute. With a view to correlating observed effect on the optically active solute with the dipole moment of the solvent, it was proposed to determine the rotatory power of d-sec- β-octyl hydrogen phthalate and d-sec- β-octyl methyl phthalate in various solvent types, in the hope that the results would yield some information concerning the general problem of solvent effect.

Experimental.

Solvents.

The purest available solvents were used as starting materials and were then treated as follows:

(a.) Nitromethane, methyl iodide, methylene chloride, carbon tetrachloride, carbon disulphide, benzaldehyde, anisole, (gave no phenol reaction), chlorobenzene, bromobenzene, iodobenzene, o-dichlorobenzene (previously cooled to -20° to freeze out traces of p-dichlorobenzene.)

Washed, dried over calcium chloride and fractionated.

(b.) Acetonitrile, acetaldehyde, acetone, ("purified by bisulphite"), aniline, ("from sulphate"), toluene.

Dried and fractionated.

(c.) Acetic acid, m.p. 16°; benzonitrile, m.p. -12.9°; nitrobenzene, m.p. $5.6 - 5.7^{\circ}$; acetophenone, m.p. 20°; benzene, m.p. 5.5°.

Purified by repeated partial freezing, followed by drying and fractionation.

(d.) Hexane, ("free from aromatic hydrocarbons") was dried and fractionated; alcohols, (methyl and ethyl), dried over lime and fractionated.

e. Chloroform was shaken with concentrated sulphuric acid, washed several times with dilute sodium hydroxide and finally with water. It was then dried over annydrous potassium carbonate and fractionated. (The method is due to Hentzsel and Hoffmann, Ber., 44, 1777, 1911).

The d-sec-β-octyl hydrogen phthalate used in this investigation wasprepared by the standard method and had $[M]^{20^\circ}_{5461} = 162.0^\circ$ in a 2 dm. tube, (alcohol, c = 5).

Preparation of d-sec-β-octyl Methyl phthalate.

20 gms. of d-octyl hydrogen phthalate were converted into the sodium salt by titration in alcohol solution with sodium ethoxide, using phenolphthalein as outside indicator. The alcohol solution of the sodium salt was then evaporated to dryness in a vacuum desiccator. The finely ground, dry product was dissolved in water, and an aqueous solution of silver nitrate added in slight excess of the calculated quantity. The resulting precipitate of silver phthalate was filtered at the pump and thoroughly washed with water; finally the salt was dried in vacuo, light being excluded. The dry silver phthalate was then treated with excess of methyl iodide,

which had been dried over calcium chloride, the iodide being added in small quantities and the whole thoroughly shaken after each addition. This precaution is necessary, since the reaction developes considerable heat if carried through too quickly. After one day (5-6 hours) in a mechanical shaker, the reaction mixture was extracted with sodium-dried ether, and the resulting ethereal solution of methyl ester filtered free from silver iodide. The ether solution was washed with aqueous sodium carbonate containing a little sodium hydroxide, then several times with water and finally dried over calcium chloride. The ether was removed in vacuo and the methyl ester kept in a vacuum desiccator at 30-40° for one day to remove the last traces of excess methyl iodide. Owing to instability at high temperatures, the diester cannot be distilled; it was therefore employed without further purification.

The d-sec-β-octyl methyl phthalate, prepared as above, had $\alpha_{5461} = 42.47^{\circ}$ in a 1 dm. tube at 20° (homogeneous).

The phthalate and methyl ester were examined in various solvents, the results being given below. All rotations are arranged in order of descending magnitude.

d-sec-β-Octyl Hydrogen Phthalate in Methane Type Solvents.

Solvent	l	c	α_{5461}	$[M]^{20^\circ}_{5461}$	Dipole moment of solvent. $\mu \times 10^{18}$ e.s.u.
C_2H_5OH	2	5.024	5.85°	162.0°	1.72 ①
CH_3OH	"	5.004	5.56°	154.6°	1.73 ①
CH_3I	"	5.024	5.48°	151.8°	1.66 ①
CCl_4	"	4.012	4.32°	149.8°	0 ②
$CHCl_3$	"	5.000	5.38°	149.7°	1.10 ②
CH_3CHO	"	5.000	5.15°	143.3°	2.72 ①
CS_2	"	5.000	5.10°	141.9°	0 ②
CH_2Cl_2	"	5.000	5.05°	140.5°	1.61 ③
$CH_3CO.CH_3$	"	5.000	5.04°	140.3°	2.97 ①
CH_3COOH	"	5.000	4.98°	138.6°	0.74 ④
CH_3CN	"	5.020	4.89°	135.6°	3.94 ①
CH_3NO_2	"	1.014	0.92°	126.2°	3.78 ①

For the most part, the rotations were determined in 5% solutions, but in the case of carbon tetrachloride and nitromethane it was not possible to obtain this concentration.

d-sec-β-Octyl Hydrogen Phthalate in Benzene Type Solvents.

Solvent	l	c	α_{5461}	$[M]^{20°}_{5461}$	Dipole moment of solvent. $\mu \times 10^{18}$ e.s.u.
$C_6H_5CH_3$	2	5.020	5.43°	150.5°	0.52 ②
C_6H_6	"	5.000	5.21°	145.0°	0 ①
$C_6H_5OCH_3$	"	5.004	4.53°	126.0°	1.16 ⑤
C_6H_5Br	"	5.000	4.26°	118.6°	1.5 ⑥
C_6H_5I	"	5.000	4.21°	117.2°	1.25 ④
C_6H_5Cl	"	5.000	4.15°	115.5°	1.55 ②
$C_6H_5NH_2$	"	5.018	3.87°	107.3°	1.51 ⑤
$o\text{-}C_6H_4.Cl_2$	"	5.000	3.76°	104.6°	2.25 ⑨
C_6H_5CN	"	5.000	2.88°	80.2°	3.84 ⑩
$C_6H_5NO_2$	"	5.016	2.83°	78.5°	3.90 ②
* C_6H_5CHO	"	5.000	2.74°	76.3°	2.75 ⑥
† C_6H_5CHO	"	5.000	2.67°	74.3°	"
$C_6H_5.CO.CH_3$	"	5.020	3.96°	109.8°	2.97 ⑧

* With freshly distilled C_6H_5CHO. † With C_6H_5CHO several days after distillation.

The value of $[M]^{20°}_{5461}$, in acetophenone shows the effect of screening the keto- group in benzaldehyde; this point will be discussed later.

In the foregoing tables, the encircled figures refer to the papers from which the dipole moment values were obtained. The references in question are given on p. 110..

d-sec-β-Octyl Methyl Phthalate in Methane Type Solvents.

Solvent	ℓ	c	α_{5461}	$[M]^{20°}_{5461}$	Dipole moment of solvent. $\mu \times 10^{18}$ e.s.u.
C_6H_{14} (Hexane)	2	5.050	4.90°	141.8°	0 ②
CH_3CHO	"	5.046	4.73°	137.0°	2.72
C_2H_5OH	"	5.048	4.65°	134.6°	1.72
CH_3COOH	"	5.044	4.58°	132.7°	0.74
$CH_3.CO.CH_3$	"	5.050	4.56°	131.9°	2.97
CH_3I	"	5.052	4.54°	131.3°	1.66
CH_3OH	"	5.040	4.48°	129.9°	1.73
CH_3CN	"	5.036	4.41°	127.9°	3.94
CH_3NO_2	"	5.042	4.24°	122.9°	3.78
CH_2Cl_2	"	5.054	3.95°	114.2°	1.61
CCl_4	"	5.040	3.78°	109.6°	0
$CHCl_3$	"	5.040	3.76°	109.0°	1.10
CS_2	"	5.050	3.22°	93.2°	0

d-sec-β-Octyl Methyl Phthalate in Benzene Type Solvents.

Solvent	l	c	α_{5461}	$[M]^{20°}_{5461}$	Dipole moment of solvent, $\mu \times 10^{18}$ e.s.u.
$C_6H_5CH_3$	2	5.040	3.87°	112.2°	0.52
$C_6H_5OCH_3$	"	5.048	3.71°	107.4°	1.16
C_6H_6	"	5.048	3.60°	104.2°	0
C_6H_5Br	"	5.052	3.07°	88.8°	1.5
$C_6H_5NH_2$	"	5.040	3.06°	88.7°	1.51
C_6H_5I	"	5.044	3.02°	87.5°	1.25
C_6H_5Cl	"	5.046	2.99°	86.6°	1.55
$O\text{-}C_6H_4Cl_2$	"	5.044	2.76°	80.0°	2.25
C_6H_5CHO	"	5.050	2.72°	78.7°	2.75
C_6H_5CN	"	5.048	2.64°	76.4°	3.84
$C_6H_5NO_2$	"	5.052	2.58°	74.6°	3.90
$C_6H_5.CO.CH_3$	"	5.052	3.45°	99.8°	2.97

The value in acetophenone is included for purposes of comparison, as before.

Discussion of Results.

The rotatory power of d-sec-β-octyl hydrogen phthalate was first investigated in solvents of the methane type. The results are given below, the rotations being arranged in descending order of magnitude. In this, and in the following tables, the dipole moments of the solvents are included for purposes of comparison.

Table I.

Rotatory Power of d-sec-β-Octyl Hydrogen Phthalate in Methane Type Solvents.

Solvent	$[M]^{20^\circ}_{5461}$	Dipole Moment of Solvent $\mu \times 10^{18}$ e.s.u.
C_2H_5OH.	162.0°	1.72
CH_3OH.	154.6°	1.73
CH_3I.	151.8°	1.66
CCl_4.	149.8°	0
$CHCl_3$.	149.7°	1.10
CH_3CHO.	143.3°	2.72
CS_2.	141.9°	0
CH_2Cl_2.	140.5°	1.61
$CH_3.CO.CH_3$.	140.3°	2.97
CH_3COOH.	138.6°	0.74
CH_3CN	135.6°	3.94
CH_3NO_2.	126.2°	3.78

A study of the above series shows that little obvious relation exists between the dipole moments of the

solvents and their effect on the rotatory power, although the tendency possibly exists for solvents of high dipole value to produce the greatest depression in rotation.

As will be seen later, however, the study of solvent effect involves a consideration of various complicating factors, the influence of which may probably account for many of the apparent displacements.

In direct contrast to the above is the series obtained in the case of the benzene type solvents, in which the rotations may be arranged, almost without exception, in the order of polarity of the solvents.

Table II.

Rotatory Power of d-sec-β-Octyl Hydrogen Phthalate in Benzene Type Solvents.

Solvent	$[M]^{20}_{5461}$	Dipole Moment of Solvent. $\mu \times 10^{18}$ e.s.u.
$C_6H_5CH_3$.	150.5°	0.52.
C_6H_6.	145.0°	0
$C_6H_5OCH_3$.	126.0°	1.16
C_6H_5Br	118.6°	1.50
C_6H_5I	117.2°	1.25
C_6H_5Cl.	115.5°	1.55
$C_6H_5NH_2$.	107.3°	1.51
$O\text{-}C_6H_4.Cl_2$.	104.6°	2.25
C_6H_5CN.	80.2°	3.84
$C_6H_5NO_2$.	78.5°	3.90
*C_6H_5CHO.	76.3°	2.75
†C_6H_5CHO	74.3°	"

*With freshly distilled C_6H_5CHO

†With C_6H_5CHO several days after distillation.

A striking relation thus emerges between dipole moment of the solvent and effect on the rotatory power.

The low value recorded in the case of benzaldehyde is probably due to the presence of traces of benzoic acid in this solvent.

The investigation of the rotatory power of d-sec-β-octyl methyl phthalate in solvents of the methane series yielded results somewhat similar to those obtained in the case of the hydrogen compound. (Table I).

Table III.

Rotatory Power of d-sec-β-Octyl Methyl Phthalate in Methane Type Solvents.

Solvent	$[M]^{20°}_{5461}$	Dipole Moment of Solvent. $\mu \times 10^{18}$ e.s.u.
C_6H_{14}. (Hexane)	141.8°	0
CH_3CHO	137.0°	2.72
C_2H_5OH	134.6°	1.72
CH_3COOH	132.7°	0.74
$CH_3.CO.CH_3$	131.9°	2.97
CH_3I.	131.3°	1.66
CH_3OH	129.9°	1.73
CH_3CN	127.9°	3.94
CH_3NO_2	122.9°	3.78
CH_2Cl_2	114.2°	1.61
CCl_4	109.6°	0
$CHCl_3$	109.0°	1.10
CS_2	93.2°	0

In this case, however, practically no trace of a definite polar effect can be seen.

Table IV.

Rotatory Power of d-sec-β-Octyl Methyl Phthalate in Benzene Type Solvents.

Solvent	$[M]^{20^\circ}_{5461}$	Dipole Moment of Solvent. $\mu \times 10^{18}$ e.s.u.
$C_6H_5CH_3$.	112.2°	0.52
$C_6H_5OCH_3$.	107.4°	1.16
C_6H_6	104.2°	0
C_6H_5Br.	88.8°	1.5
$C_6H_5NH_2$	88.7°	1.51
C_6H_5I.	87.5°	1.25
C_6H_5Cl	86.6°	1.55
$O\text{-}C_6H_4\text{-}Cl_2$	80.0°	2.25
C_6H_5CHO	78.7°	2.75
C_6H_5CN	76.4°	3.84
$C_6H_5NO_2$	74.6°	3.90

The correlation of the results in the case of the methane solvents is a matter of some difficulty, the lack of any definite regularity being manifest.

A general survey of the investigation, however, would undoubtedly appear to lead to the idea that a definite relationship exists between dipole moment of the solvent and effect on the rotatory power of an optically active solute.

While the experimental work is realised to be scarcely comprehensive enough to admit of definite

conclusions, it is tentatively suggested* that one of the main factors governing the influence of solvents on rotatory power is the influence exerted by the solvent dipoles upon the external field of the solute molecules, the effect acting either through deformation or dipole association.

This supposedly main effect may, however, be modified to some extent by such factors as characteristic structure and degree of association of the solvent molecules.

An interesting survey of the results is afforded in the light of the above suggestions.

Thus, in the case of d-sec-β-octyl hydrogen phthalate in methane solvents, (Table I) the greatest depressive influence is exerted by the two most polar types, a tendency to exalt being observed with the non-polar solvents. The comparison is by no means complete, however, the highest rotations being obtained in comparatively polar types, namely, methyl and ethyl alcohols.

It seems possible that some of the divergences may be due to combination between the solute and the solvent molecules, this holding especially in the case of acetic acid and the alcohols.

The investigation of the rotatory power of d-sec-β-octyl methyl phthalate leads to results similar to those obtained in the case of the hydrogen compound.

* Compare Rule & McLean, J.C.S., 1931. (March number, in the press).

In solvents of methane type, however, practically no regularity at all was evinced (Table III).

The low rotations exhibited in carbon tetrachloride and carbon disulphide are reminiscent of the effects obtained by Pickard and Kenyon[1.] and Rule and Mitchell[2.] in the case of the d-octyl esters of acetic and monosubstituted acetic acids, for which, however, some regularities were observed with benzene solvents. (See Introduction p.73).

The relative positions of acetic acid in the two methane series is a matter of some interest; it seems feasible that the difference may be attributed to the presence of the -COOH group, common, in the instance of the hydrogen compound, to both solute and solvent.

The effects observed for the phthalate and methyl ester in benzene solvents, (Tables II & IV) offer a most remarkable contrast to those discussed above, the regularity of relation between dipole moment of the solvent and observed influence on the rotatory power holding almost without exception.

The marked difference between the results for the methane and benzene series is difficult of explanation, but an additional cause of irregularity in the methane types may be the lack of structural similarity in the various solvents employed. In benzene, the molecule is so large that the presence

of a small substituent causes much less relative change in form and volume than in the case of methane.

An interesting comparison is obtained by a consideration of the results in the case of the solvents benzaldehyde, C_6H_5CHO and acetophenone, $C_6H_5.CO.CH_3$.

d-sec-β-Octyl Hydrogen Phthalate.

Solvent	$[M]^{20^\circ}_{5461}$	D.M. of Solvent $\mu \times 10^{18}$ e.s.u.
$C_6H_5CO.CH_3$	109.8°	2.97
C_6H_5CHO	74.3°	2.75

d-sec-β-Octyl Methyl Phthalate.

Solvent	$[M]^{20^\circ}_{5461}$
$C_6H_5.CO.CH_3$	99.8°
C_6H_5CHO	78.7°

Thus, in spite of its greater polarity, acetophenone exerts decidedly less influence than does benzaldehyde.

It would seem, however, that the discrepancy may be explained by the assumption that the -CO dipole, common to both solvents, is, in the case of acetophenone, "screened" by the alkyl group, the influence of this solvent on an optically active solute being therefore proportionately reduced.

Recent research would appear to indicate

that a fundamental relationship exists between the study of optical activity and that of absorption spectra.

In this connection may be mentioned the investigations of Lowry and others on the Drude equation and the successful asymmetric decomposition of racemic compounds effected by W. Kuhn[11.] and S. Mitchell[12.] by the use of circularly polarised light, following an examination of the absorption data.

Of great interest, therefore, is the work of G. Scheibe,[13.] who has investigated the screening of the CO- dipole by alkyl groups and the polar influence of solvents on ketones by means of the absorption spectra.

This author finds that the effect of solvents of increasing polarity is to displace the characteristic absorption band of a ketone progressively towards the far ultra-violet.

The polar series in the case of acetone is as follows:-

Carbon tetrachloride, hexane, ether, ethylacetate, chloroform, methylene chloride, ethyl alcohol, methyl alcohol, acetic acid, water.

→

Displacement towards shorter wave-length.

A point of some importance, from the viewpoint of comparison with optical activity effects, is that the

magnitude of the observed displacement diminishes progressively as the carbonyl group becomes more and more screened by substitution in the adjacent CH_3 group; the order of solvents, however, remains unchanged. Thus, the shift of the characteristic band is less for tertiary-butyl ketone than for acetone and still less for hexamethyl acetone.

These changes present an interesting parallel to the previously discussed effects obtained in the field of optical activity.

If we assume the validity of the Drude equation in the case of an optically active keto-compound, the aforementioned displacement of the absorption band corresponds to a fall in rotatory power with increasing polarity of solvent.

Appendix.

d-Sec-β-octyl anthranilate was prepared with a view to examining the variation of the rotatory power of the hydrochloride with concentration in ethyl alcohol solution. It was found, however, that the value obtained in alcohol (c = 5) for the hydrochloride differed somewhat from that previously determined for the corresponding l-compound. (Rule, Miles and MacGillivray, J.C.S., 2275, 1929).

The difference was attributed to the fact that in the case of the l-ester ordinary absolute alcohol had been used as solvent, whereas in the present investigation the alcohol employed was dried over calcium filings and fractionated. As described later, experiments involving addition of known amounts of water to the anhydrous alcohol were carried out.

In addition to the above, d-sec-β-octyl p-amino-benzoate and d-sec-β-octyl o-dimethylamino-benzoate were prepared and the rotatory powers of the hydrochlorides determined in alcohol solution. In both cases the values obtained showed good agreement with those previously quoted. (J.C.S., 2275, 1929).

Experimental.

Preparation of Methyl Anthranilate.

200 gms. anthranilic acid (m.p. 143-144°) were dissolved in excess methyl alcohol (2 litres). The solution was then heated on the water-bath for 48 hours under a reflux condenser carrying a calcium chloride tube. The flask was fitted with a two-way stopper and a rapid current of dry hydrogen chloride was bubbled through the liquid. The reaction product containing the hydrochloride of the ester and any unchanged acid was poured into an excess of sodium carbonate solution, when the ester separated in oily globules. The whole was then extracted with ether, the ethereal solution evaporated to half-bulk and allowed to stand for several days over anhydrous potassium carbonate.

The remainder of the ether was thereafter removed and the ester distilled under reduced pressure. At 8 mm. a pale yellow fluid was obtained, b.p. 125°. On standing in a refrigerator, this solidified to a pale yellow mass. Upon recrystallisation from ligroin, the ester appeared as a white crystalline solid, m.p. 24- 25°.
(E.& H. Erdmann, Ber., 32, 1216, 1899, quote 24.5°).
About 140 gms. pure methyl anthranilate were obtained.

Preparation of d-sec-β-Octyl Anthranilate.

The anthranilate was prepared by the method of Rule, Miles and MacGillivray, (J.C.S., 2274,1929), using 14 gms. d-octyl alcohol, 0.15 gm. sodium and 16.5 gms. methyl anthranilate.

Yield of pure ester, 10 gms. (b.p. 178° at 7 mm.).

The following is the summary of the rotations determined.

Rotatory Power of d-Octyl Anthranilate.*

Solvent	l	c.	α_{6708}	α_{5893}	α_{5461}	α_{4358}	$[M]^{20°}_{6708}$	$[M]^{20°}_{5893}$	$[M]^{20°}_{5461}$	$[M]^{20°}_{4358}$
Ethyl alcohol	1	5.220	-	-	0.46°	-	-	-	22.0°	-
Ethyl alcohol + 1 molecular proportion of HCl	1	5.012	0.97°	1.22°	1.42°	2.35°	48.2°	60.6°	70.6°	116.9°

It is to be noted that the aforementioned divergence was noted only in the case of the hydrochloride; the rotatory power of the ester in alcohol solution showed good agreement with the previously determined value for the l-compound.

* See graphs p.100.

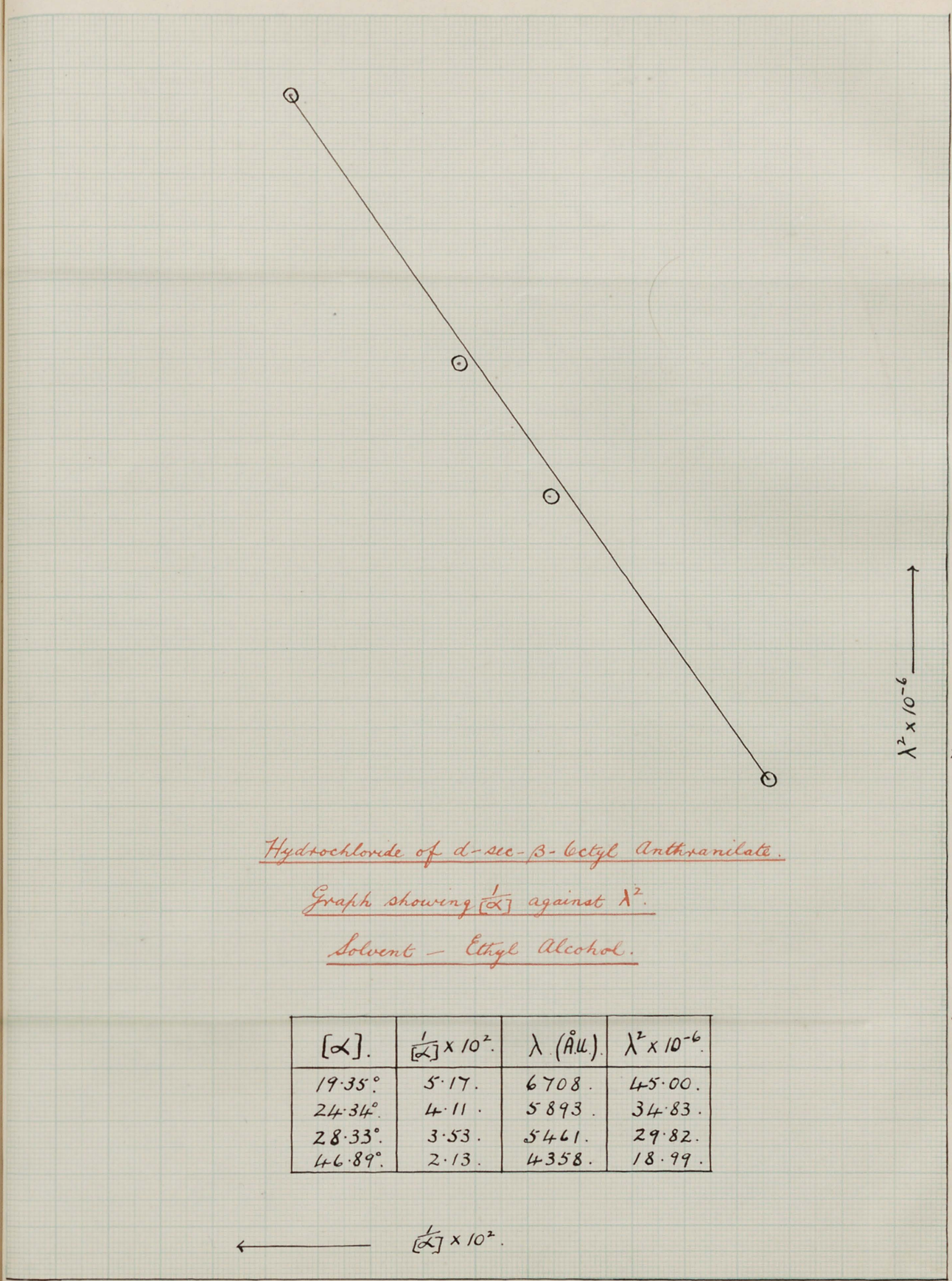
d-sec-β-Octyl Anthranilate Hydrochloride in Alcohol (Varying water - content). *

Solvent	l	c	α_{5461}	$[M]^{20°}_{5461}$
Alcoholic HCl (anhydrous alcohol)	1	5.034	1.45°	71.8°
Alcoholic HCl (ordinary absolute alcohol)	"	5.044	1.34°	66.2°
† (alcohol containing 1% water by vol.)	"	5.028	1.10°	62.5°
Alcoholic HCl (alcohol containing 2% water by vol.)	"	5.052	1.15°	56.7°
Alcoholic HCl (alcohol containing 4% water by vol.)	"	5.130	1.05°	51.0°

In most of the above determinations, the hydrochloride was obtained in solution by the addition of the calculated volume of previously standardised alcoholic HCl to a known weight of the ester in alcohol solution. In all cases, the alcoholic HCl was made up using the same alcohol as was employed to dissolve the ester and make up the solution.

† In this determination the solid hydrochloride, (m.p. 160-161°), was employed.

* See graphs p. 101.



Hydrochloride of d-sec-β-octyl Anthranilate.

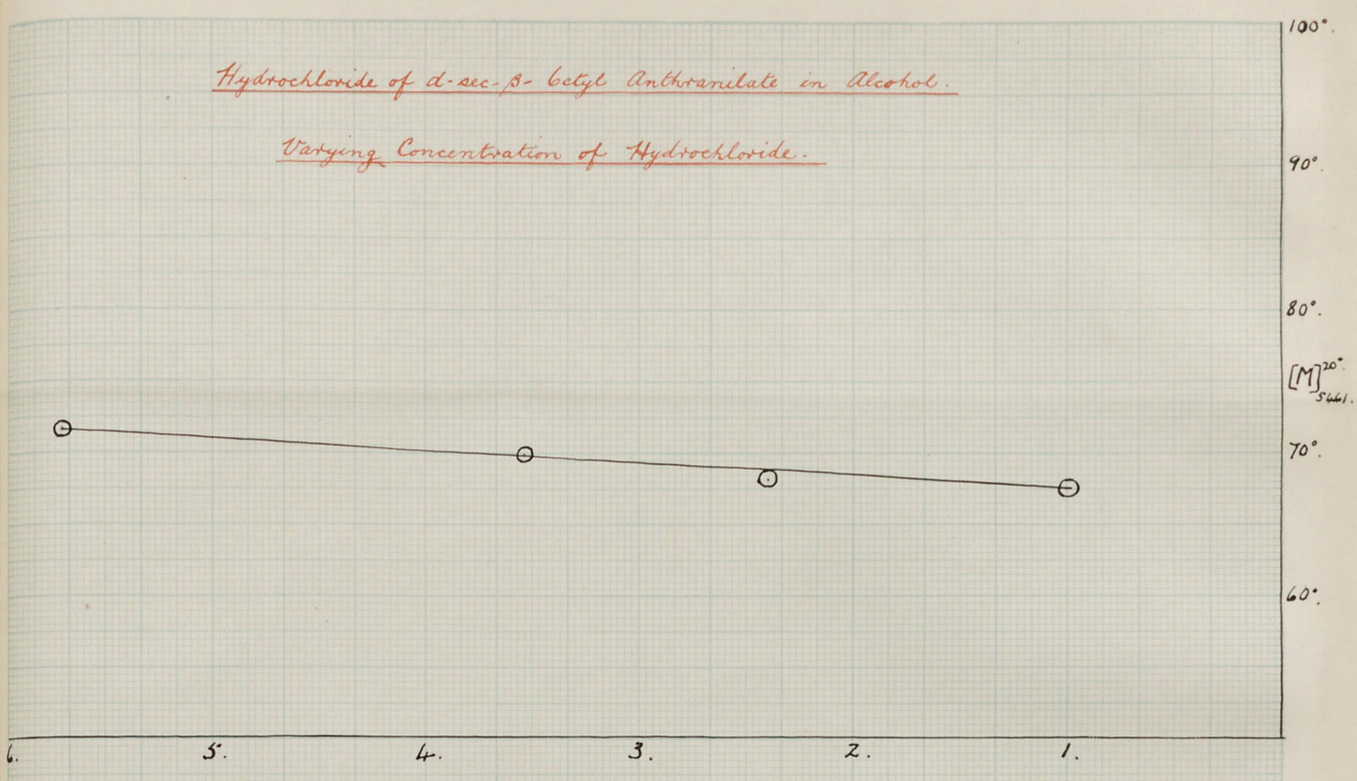
Graph showing $\frac{1}{[\alpha]}$ against λ^2.

Solvent – Ethyl Alcohol.

$[\alpha]$.	$\frac{1}{[\alpha]} \times 10^2$.	λ (Å.U.).	$\lambda^2 \times 10^{-6}$.
19·35°.	5·17.	6708.	45·00.
24·34°.	4·11.	5893.	34·83.
28·33°.	3·53.	5461.	29·82.
46·89°.	2·13.	4358.	18·99.

Hydrochloride of d-sec-β-octyl Anthranilate in Alcohol.

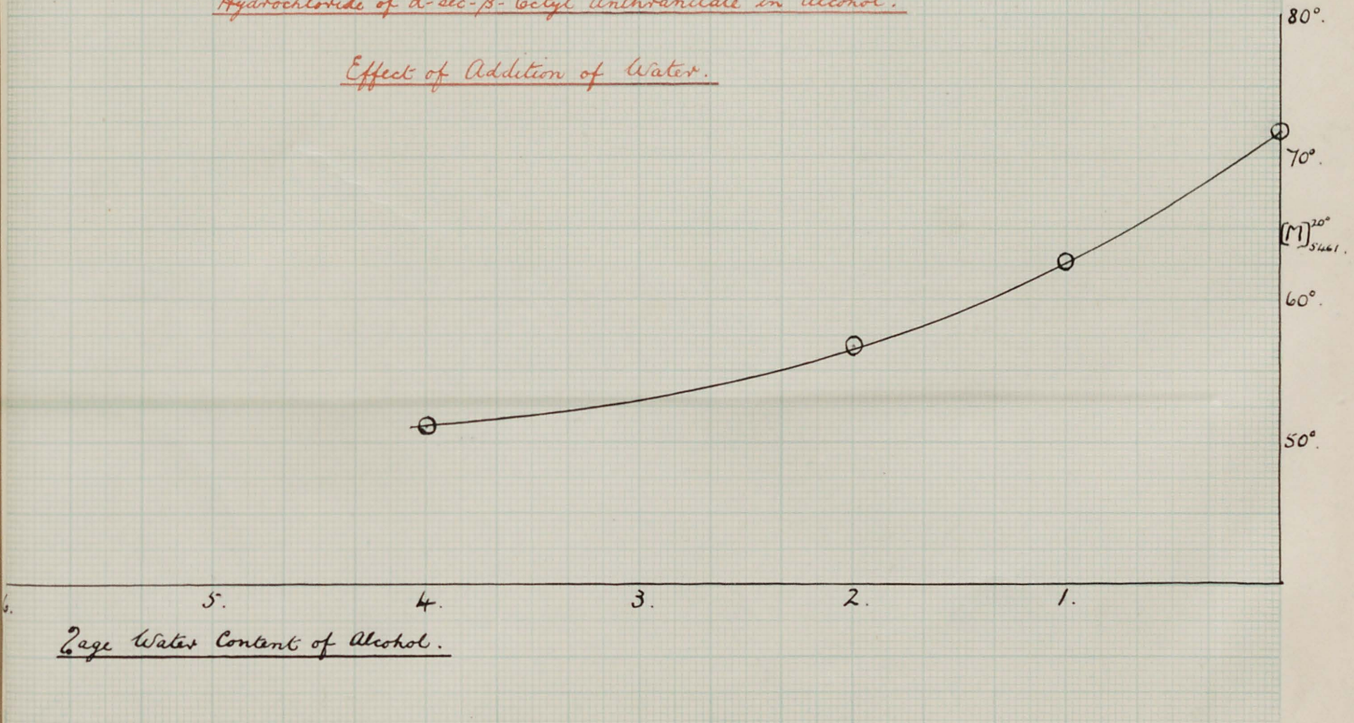
Varying Concentration of Hydrochloride.



Concentration of Hydrochloride. (Gms./100 c.c.)

Hydrochloride of d-sec-β-octyl Anthranilate in Alcohol.

Effect of Addition of Water.



Gage Water Content of Alcohol.

d-sec-β-Octyl Anthranilate Hydrochloride in alcohol.

(Varying concentration of hydrochloride).*

Solvent	l	c	α_{5461}	$[M]^{20^\circ}_{5461}$
Ethyl alcohol	4	1.006	0.95°	67.5°
" "	1	2.431	0.58°	68.2°
" "	"	3.562	0.87°	69.8°
" "	"	5.731	1.45°	71.8°

The above investigation was somewhat restricted owing to the unexpectedly low solubility of the hydrochloride in alcohol.

* See graphs p.101.

Preparation of d-sec-β-Octyl p-Amino-benzoate.

This compound was prepared by the method of Rule and Miles (loc.cit.), using 0.2 gm. sodium, 18 gms. octyl alcohol and 20 gms. methyl p-amino-benzoate. The methyl p-amino-benzoate was previously recrystallised from 60-80° petrol ether until pure (m.p. 112°).

The crude octyl ester was fractionated in vacuo, the fraction boiling between 160-180°/0.2 mm. being collected. The distillate solidified on cooling and the white solid so obtained was recrystallised from a mixture of petrol ether and ligroin until optically pure. About 6 gms. of the pure ester were obtained.

The following determinations of rotatory power were made.

Rotatory Power of d-sec-β-Octyl p-Amino-benzoate.

Solvent	l	c	α_{5461}	$[M]^{20^\circ}_{5461}$
Ethyl Alcohol	1	4.316	2.79°	161.1°
Alcoholic HCl (annydrous alcohol)	"	4.050	1.81°	111.4°
Alcoholic HCl (alcohol containing 5% water by volume)	"	4.050	2.02°	124.4°

Preparation of Methyl Methylamino-benzoate.

The preparation was started from crude mono-methylamino-benzoic acid, prepared from anthranilic acid. The crude acid was recrystallised twice from alcohol, the pure product melting at 177°.

The methyl ester was obtained from the acid in the usual manner, using hydrogen chloride as catalyst. It distilled as a pale yellow oil, (b.p. 130-135°/14 mm.) which solidified on cooling. m.p. of solid, 15°. Yield of ester, 30 gms.

Preparation of Methyl Dimethylamino-benzoate.

The methyl ester, obtained as above, was heated on the water-bath with exactly one equivalent of methyl iodide. The reaction was carried out in a pressure bottle, heating being continued for

two hours. The hydriodide of the ester so obtained was washed at the pump with ether and was a pale yellow solid, m.p. 159°. It was added to the theoretical amount of sodium carbonate solution and the free ester liberated. This was extracted with ether and the extract dried over anhydrous sodium sulphate for several days. The ether was then removed and the ester distilled under reduced pressure. It was obtained as a yellow oil, b.p. 134-135°/18 mm. and had very little odour. Unlike the mono-methylamino ester, it did not solidify upon cooling.

About 20 gms. of the pure ester were obtained.

Preparation of d-sec- β-Octyl o-dimethylamino-benzoate.

This preparation was carried out using 0.14 gm. sodium, 11 gms. d-octyl alcohol and 15 gms. methyl o-dimethylamino-benzoate. Distillation of the crude octyl ester yielded two fractions, the first (b.p. 85-90°/0.2 mm.) being retained and the second (b.p. 125-130°/0.2 mm.) submitted to further fractionation. After three fractionations, a small quantity of the pure ester (b.p. 126°/0.2 mm.) was obtained.

Rotatory Power of d-sec-β-Octyl o-dimethylamino-benzoate.

Solvent	l	c	α_{5461}	$[M]^{20°}_{5461}$
Ethyl alcohol	1	4.844	0.55°	31.5°
Ethyl alcohol + 1 molecular proportion of HCl	"	5.424	1.40°	71.6°

Summary.

The rotatory powers of several d-octyl esters of substituted benzoic acids have been examined, with a view to determining the influence of concentration in alcoholic solution and the effect of added water.

In the case of d-sec-β-octyl anthranilate, the hydrochloride of the ester has been shown to undergo small, but definite changes with varying concentration. Owing to the small concentration changes involved, this part of the investigation was not extended further.

It has also been found that addition of water to alcohol solutions of the hydrochloride of the anthranilate causes a change in the rotation, the direction of the change being towards the value for the free ester.

A similar state of affairs exists in the case of d-sec-β-octyl p-amino-benzoate.

In conclusion, the author desires to thank Dr H.G. Rule for his encouragement and valuable guidance during the course of the research.

Optical Activity of Electrolytes.

References.

1. Ann. Chim. Phys., 3 ,59, 206.
2. Lieb. Ann., 189, 241, (1877).
3. Mem. de l'Acad., 16, 229, (1838).
4. Ber., 6, 1073, (1873).
5. Lieb. Ann., 182, 33, (1876).
6. Lieb. Ann., 197, 48, (1879).
7. Rec. trav. Chim., 4, 166, (1885).
8. Zeit. f. Phys. Chem., 12, 476, (1893).
9. J. C. S., 63, 548, (1893).
10. Lieb. Ann., 207, 257, (1881).
11. Ann. Phys., 10, 70, (1928).
12. J. P. C., 11, 207, (1907).
13. Stubbs, J. C. S., 99, 2284, (1911).
14. Zeit. f. Phys. Chem., 15, 196, (1894).
15. Zeit. f. Phys. Chem., 70, 376, (1910).
    See also Trans. Far. Soc., 15, 90, (1919).
16. Monatshefte, 53-54, 14, (1929).
17. Zeit. f. Phys. Chem., 16, 671, (1895).
18. Lieb. Ann., 207, 257, (1881).
19. J. C. S., 99, 2284, (1911).
20. Ann. Chim. Phys., [3], 82, (1844) etc.
21. Optische Drehungsvermogen, p. 220.
22. See also-Patterson, J. C. S., 3006, (1928).
23. Ber., 23, 3570, (1890).
24. Zeit. f. Phys. Chem., 9, 707, (1892).
25. Biochem. Zeitsch., 30, 357, (1911).

26. Amer. Chem. Journal, 3, 351, (1888).

27. J.C.S., 99, 2265, (1911).

28. Ber., 32, 3432, (1899).

29. J.C.S., 101, 1833, (1912).

30. Ann. Phys., 10, 70, (1928).

31. Zeit. f. Phys. Chem., 16, 671, (1895).

32. Refractometric Studies, 1924-29.

33. J.P.C., 34, 2567, (1930).

34. J.P.C., 34, 897, (1930).

35. Thesis, 1930.

36. Sidgwick, "The Electronic Theory of Valency", pp. 185-203.

37. J.A.C.S., 32, 741, (1910).

38. Lewis & Randall, Thermodynamics, p. 323.

39. " " " p. 315.

40. " " " p. 362.

41. J.A.C.S., 43, 1112, (1921).

42. Monatshefte, 53-54, 14, (1929).

43. Trans. Far. Soc., 26, 389, (1930).

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References.

1. J.C.S., 105, 835, (1914).
2. J.C.S., 3202, (1926).
3. Trans.Far.Soc., 26, 321, (1930).
4. J.C.S., 1493, (1928), & J.C.S., 2516, (1929).
5. Phil.Mag., 46, 497, (1923).
6. Phys.Zeits., 13, 97, (1912).
7. Chem.Rev., 549, (1929).
8. " " 589, (1929).
9. Thesis, Copenhagen, (1928).
10. Leipziger Vortrage, (1929).
11. Zeit.f.Phys.Chem., 7, 292, (1930).
12. J.C.S., 1892, (1930).
13. Ber., 2617,(1926).

References for Dipole Moment Values.

1. K. Höjendahl, Thesis, Copenhagen, 1928.
Ann.d.Phys., 42, 569, (1913).

2. J. W. Williams, Phys.Zeits., 29, 174, (1928).

3. P.C.Mahanti & R.N. Das Gupta, J.Ind.C.S., 6, 411,(1929).

4. K.A. Wolf & co-workers, Phys.Zeits., 31,(1930).

5. K. Höjendahl, Thesis, Copenhagen,1928.
Phys.Zeits., 30, 391, (1929).

6. J. W. Williams, Phys.Zeits.,29, 683, (1928).

7. P.Walden & O. Werner, Zeit.f.Phys.Chem., B 2,10,(1929.)

8. G. Hassel & E. Naeshagen, Zeit.f.Phys.Chem.,B 4,217,(1929.)

9. Smyth, Morgan & Boyce, J.A.C.S., 50, 1536,(1928.)

10. Smyth & W. N. Stoops, J.A.C.S., 50, 1883,(1928.)